COMPETE 2020 · PORTUGAL 2020 · UNIÃO EUROPEIA Fundo Europeu de Desenvolvimento Regional · GOVERNO DE PORTUGAL · FCT Fundação para a Ciência e a Tecnologia MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

Universidade do Minho
Escola de Ciências

LaPMET Workshop

Nanostructured plasmonic thin films for LSPR sensing applications

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Centro de Física das Universidades do Minho e do Porto, Portugal

CF-UM-UP

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INTRODUCTION — **LOCALIZED SURFACE PLASMON RESONANCE (LSPR)**

The Localized Surface Plasmon Resonance (LSPR) Phenomenon

"LYCURGUS CUP"
Au and Ag nanoparticles in glass

4th century Roman Cup
British Museum

Nanocomposite thin film containing noble metal nanoparticles dispersed in an oxide matrix

21st Century Coloured Cups With Thin Film Technology

M.S. Rodrigues, *et al.*, Appl. Sci. 2021, 11, 5388

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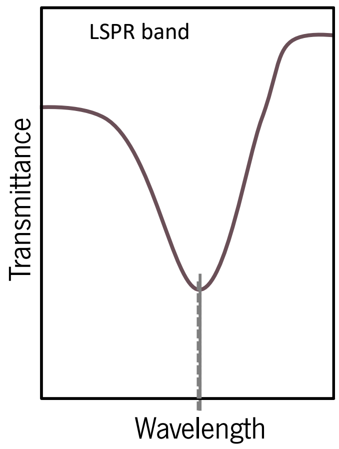
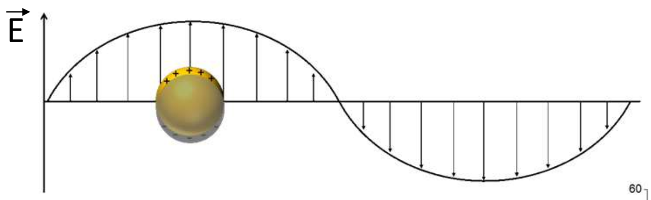
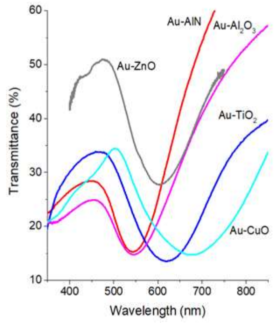
Adjusting the LSPR Band





LSPs' resonance frequency can be adjusted by changing:

- ✓ Type of plasmonic metal, Au, Ag, ...;
- ✓ Nanoparticle size, shape and distribution;
- ✓ Surrounding dielectric matrix.



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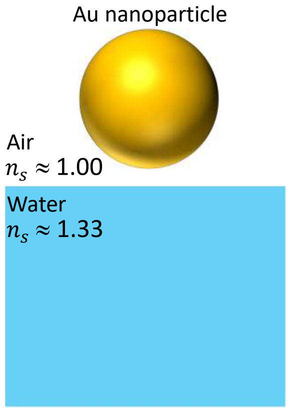
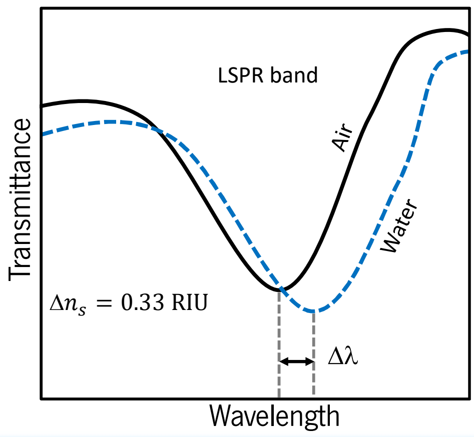
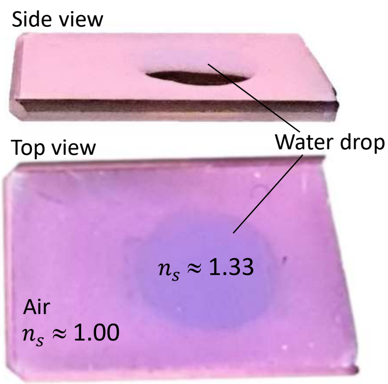
LSPR for Sensing Applications







M.S. Rodrigues, *et al.*, Appl. Sci. 2021, 11, 5388

$$\textbf{Sensitivity} = \frac{\text{Parameter shift } (\Delta\lambda)}{\text{Refractive index difference } (\Delta n_s)}$$

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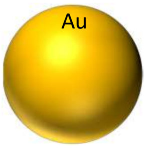
INTRODUCTION | LOCALIZED SURFACE PLASMON RESONANCE (LSPR)

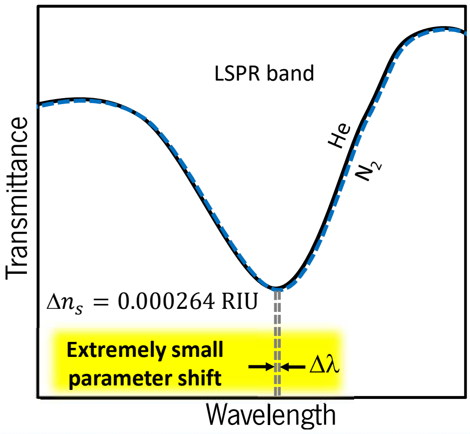
LSPR for Gas Sensing Applications

Extremely small refractive index change

Helium (He)
$n_s \approx 1.000034$



Nitrogen (N_2)
$n_s \approx 1.000298$



- ✓ Sensitivity of the thin films has to be enhanced.
- ✓ High resolution optical sensing system to enable the measurement of small changes in the LSPR band

$$\textbf{Sensitivity} = \frac{\text{Parameter shift } (\Delta\lambda)}{\text{Refractive index difference } (\Delta n_s)}$$

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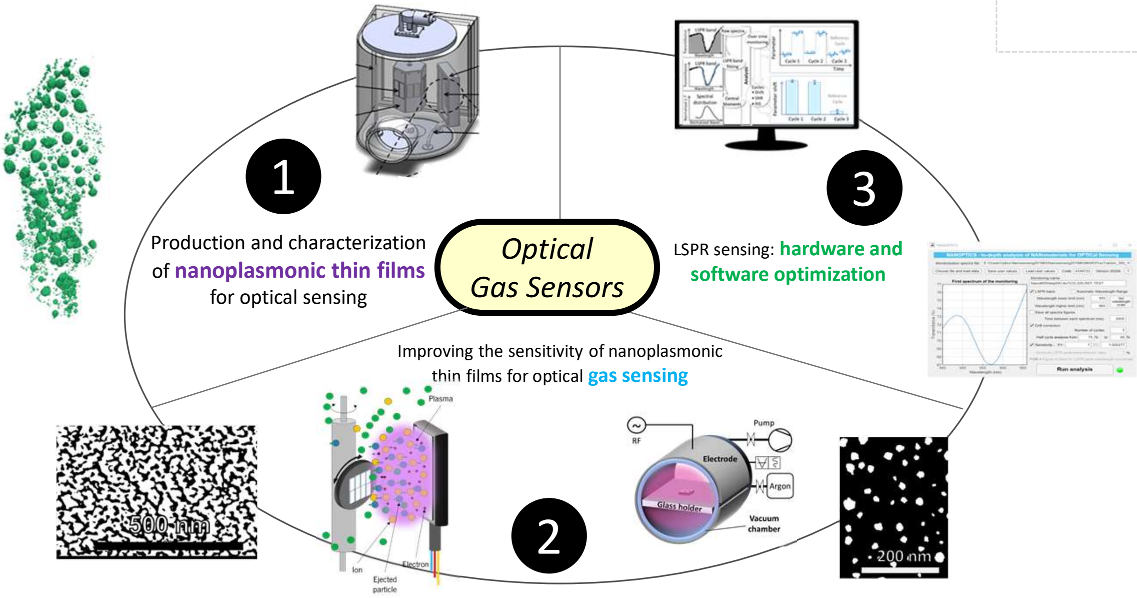
RESEARCH WORK | OBJECTIVES



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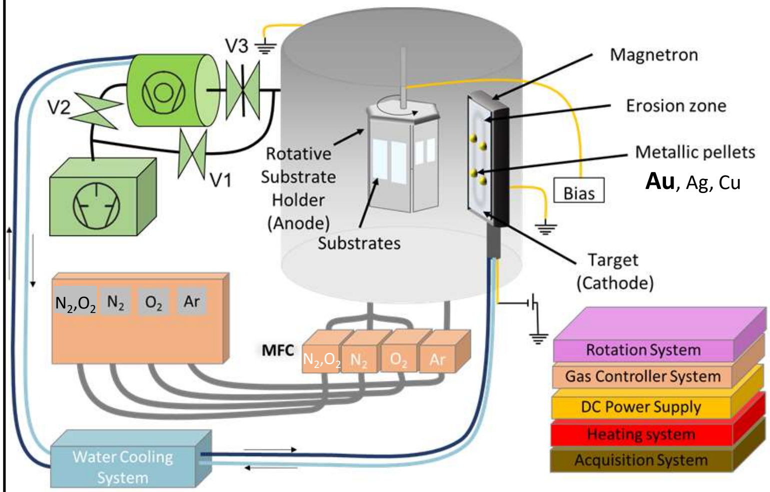
RESEARCH WORK

PRODUCTION AND CHARACTERIZATION OF AU-TIO$_2$ THIN FILMS FOR OPTICAL SENSING

Production of nanocomposite films

Reactive DC Magnetron Sputtering



- ✓ Me$_x$O$_y$; Me = **Ti**, Al, Cu, Zn;
- ✓ Noble metal pellets placed in the erosion zone of the target.

Preparation parameters:

- ✓ Deposition time:
  45, 90 and <u>150</u> min
- ✓ Au fraction area on target:
  0.3, <u>0.6</u> and 0.9 %
- ✓ Target current density:
  50, 75, <u>100</u> and 125 A.m^{-2}


Applied Surface Science
Available online 20 September 2017
In Press, Corrected Proof
ELSEVIER
Full Length Article
Optimization of nanocomposite Au/TiO$_2$ thin films towards LSPR optical-sensing

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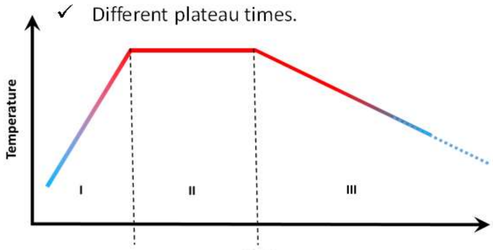
RESEARCH WORK

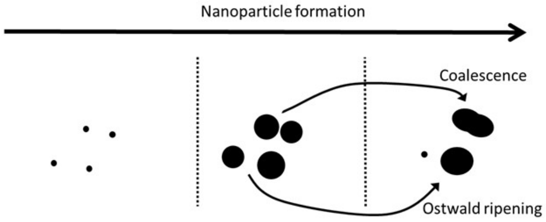
PRODUCTION AND CHARACTERIZATION OF AU-TIO$_2$ THIN FILMS FOR OPTICAL SENSING

Nanoparticle Formation

- ✓ Several annealing temperatures :
  200, 300, 400, 500, 600 and 700 °C;
- ✓ Different plateau times.



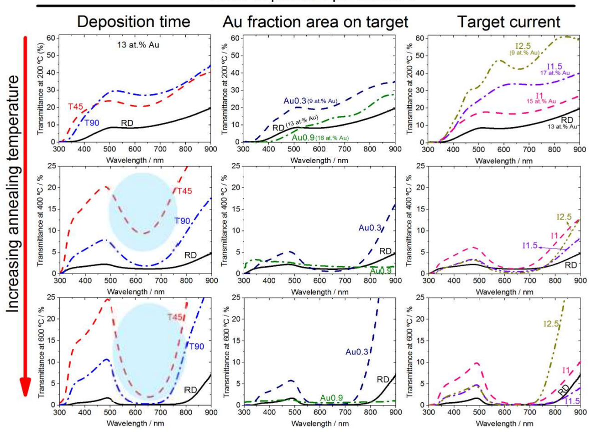
Nanoparticle formation



Au-TiO$_2$ thin film with suitable optical transmittance

LSPR band for optical sensing

Tested deposition parameters



M.S. Rodrigues, *et al*, Applied Surface Science, 2017

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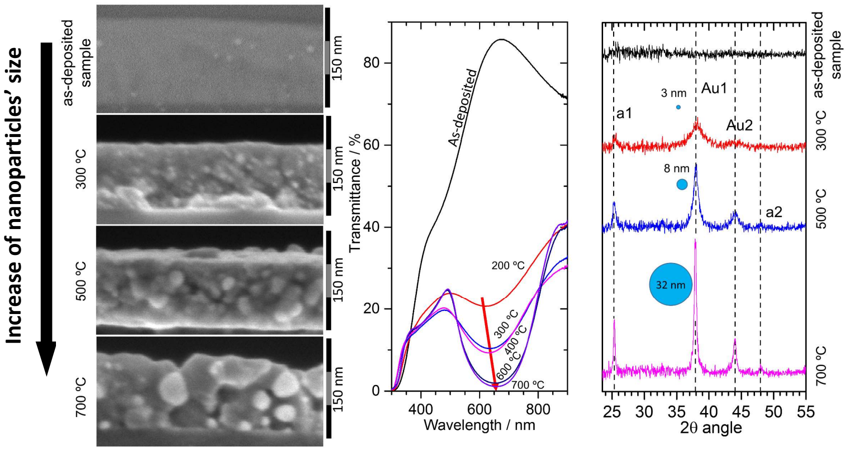
RESEARCH WORK

PRODUCTION AND CHARACTERIZATION OF Au-TiO_2 THIN FILMS FOR OPTICAL SENSING

Optical and Microstructural Characterization



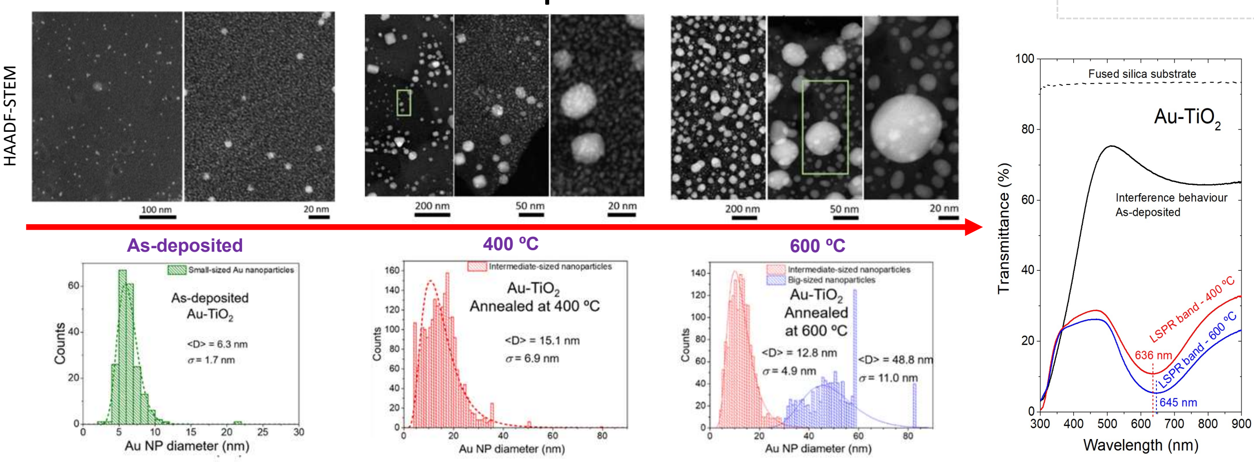
- RBS
  - In-depth atomic content.
  - [Au] = 13 at.%
- SEM
  - Thickness ≈ 100 nm
  - **Bigger nanoparticles** after increasing annealing temperature
- UV-Vis-NIR Spectroscopy
  - **More intense T-LSPR band** after increasing annealing temperature
- XRD
  - **Anatase** phase of TiO_2
  - Increasing grain size of **crystalline Au** domains

M.S. Rodrigues, *et al*, Applied Surface Science, 2017

RESEARCH WORK

PRODUCTION AND CHARACTERIZATION OF Au-TiO_2 THIN FILMS FOR OPTICAL SENSING

Nanoparticle Formation




ACS APPLIED MATERIALS & INTERFACES

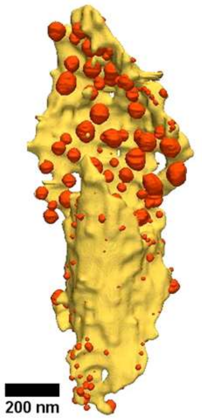
Electron Tomography of Plasmonic Au Nanoparticles Dispersed in a TiO_2 Dielectric Matrix

RESEARCH WORK

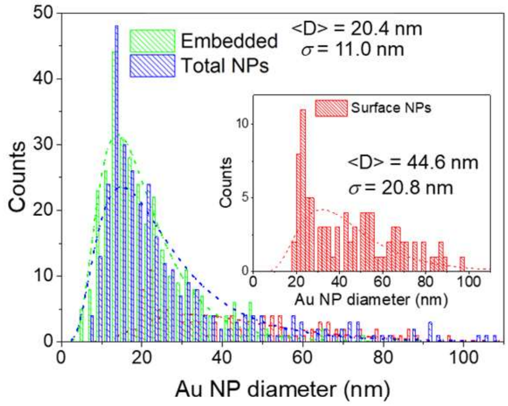
PRODUCTION AND CHARACTERIZATION OF AU-TiO_2 THIN FILMS FOR OPTICAL SENSING

3D Characterization of Nanoparticles

Electron Tomography



3D reconstruction from HAADF-STEM at several angles of Au-TiO2 at 600 °C

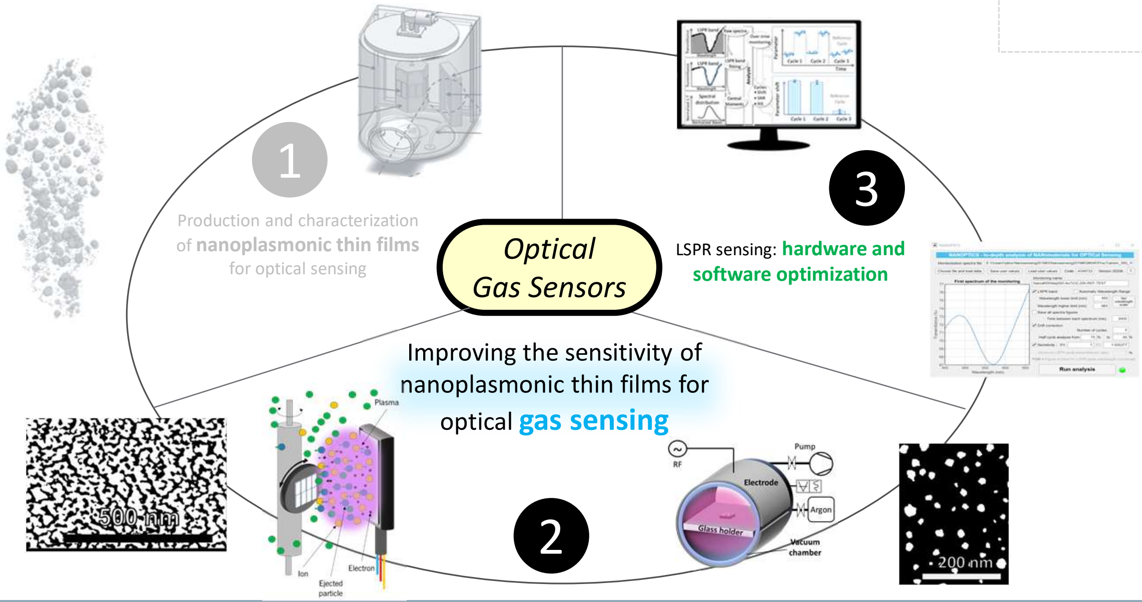


Siddardha Koneti, M.S. Rodrigues, *et al*, ACS Applied Materials and Interfaces, 2018

- ✓ 3D representation of the Au-TiO_2 thin film revealed the presence of intermediate-sized and big-sized nanoparticles, as well as their **relative positions**
- ✓ The nanoparticles at the surface have a **higher average size**

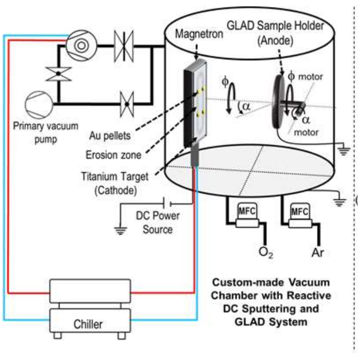
RESEARCH WORK

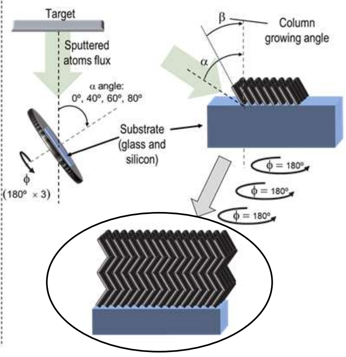
OBJECTIVES



RESEARCH WORK

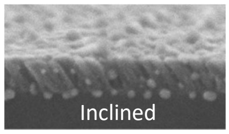
Thin films by Glancing Angle Deposition (GLAD)

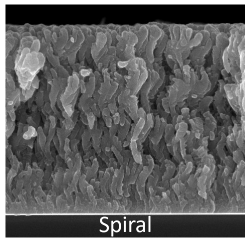




GLAD sample holder:

- ✓ mechanical parts;
- ✓ stepper engines;
- ✓ angle sensors;
- ✓ controllers
- ✓ software …

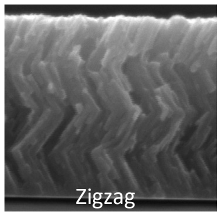


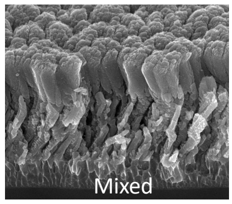


Preparation parameters:

- ✓ Architecture: **2 zigzag**
- ✓ Incidence angle α: **0°, 40°, 60° and 80°**
- ✓ Annealing temperature: **400 °C**

IOPscience
Nanotechnology
ACCEPTED MANUSCRIPT
Nanoplasmonic response of porous Au-TiO2 thin films prepared by oblique angle deposition





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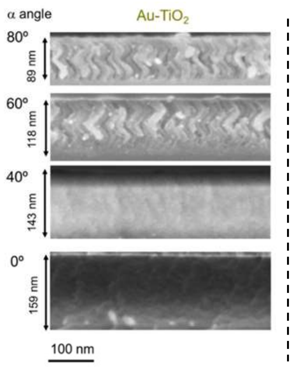
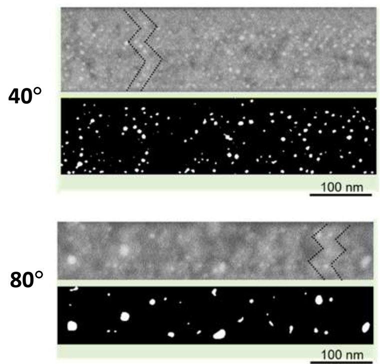
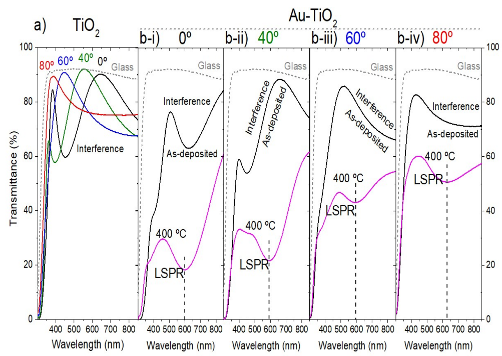
RESEARCH WORK

Optical and Microstructural Characterization







Dense and **porous zigzag architectures** were obtained

The incidence angle adjusted the porosity that **changed the nanoparticles' size distribution**

The obtained architectures produced **different optical responses** showing the LSPR band after annealing

M.S. Rodrigues, *et al.*, Nanotechnology. 30 (2019) 225701

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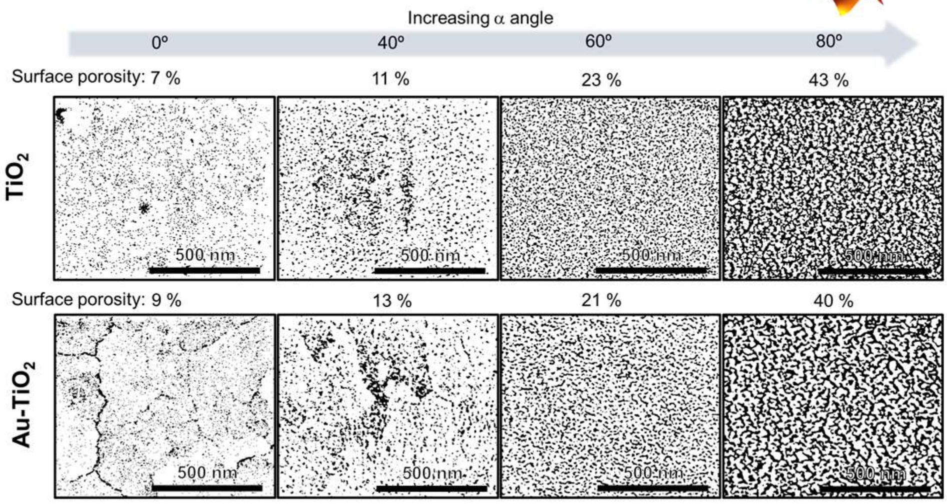
RESEARCH WORK

IMPROVING THE SENSITIVITY OF AU-TIO$_2$ THIN FILMS FOR OPTICAL GAS SENSING

Surface porosity estimation



White – thin film ; Black – porosity

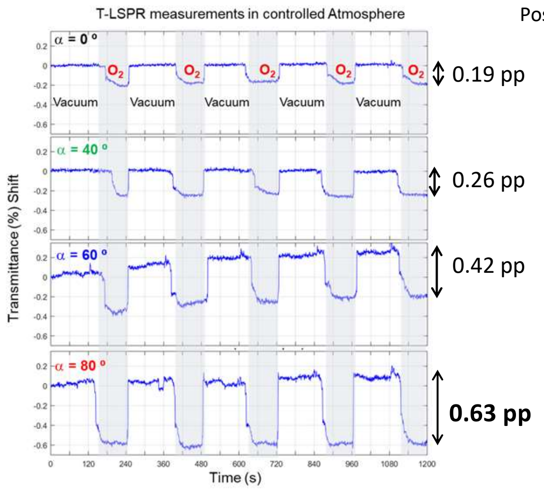
With GLAD, by increasing the incidence angle, a **surface porosity improvement** was achieved

M.S. Rodrigues, *et al.*, Nanotechnology. 30 (2019) 225701

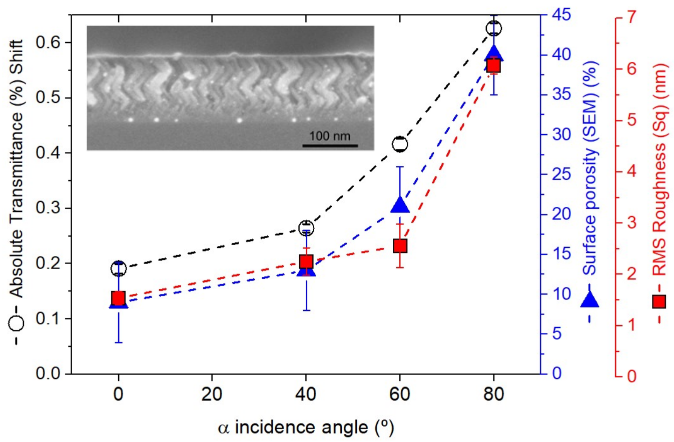
RESEARCH WORK

IMPROVING THE SENSITIVITY OF AU-TIO$_2$ THIN FILMS FOR OPTICAL GAS SENSING

T-LSPR monitoring – O_2 sensitivity



Positive correlation between **surface porosity and transmittance shift** after O_2 addition

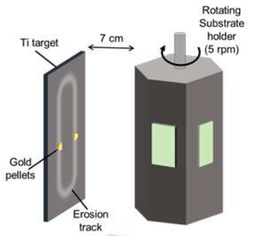


M.S. Rodrigues, *et al.*, Nanotechnology. 30 (2019) 225701

RESEARCH WORK

IMPROVING THE SENSITIVITY OF Au-TiO_2 THIN FILMS FOR OPTICAL GAS SENSING

Plasma treatments

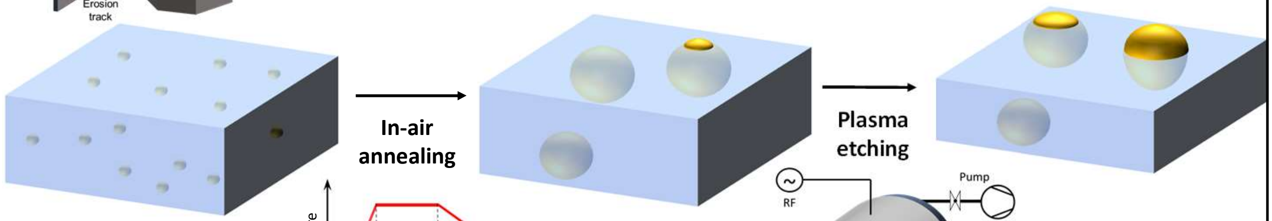


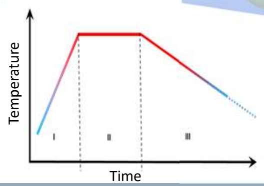
Preparation parameters:

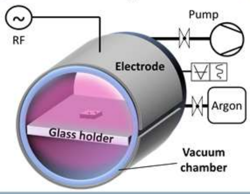
- ✓ Deposition time: 18 min
- ✓ Annealing temperature: 400 °C 5h
- ✓ **Plasma treatment: argon 60 min**

- ✓ **Semi-exposure** of nanoparticles
- ✓ **Nanoparticles anchored** to the host matrix

materials MDPI
Article
Enhancing the Sensitivity of Nanoplasmonic Thin Films for Ethanol Vapor Detection







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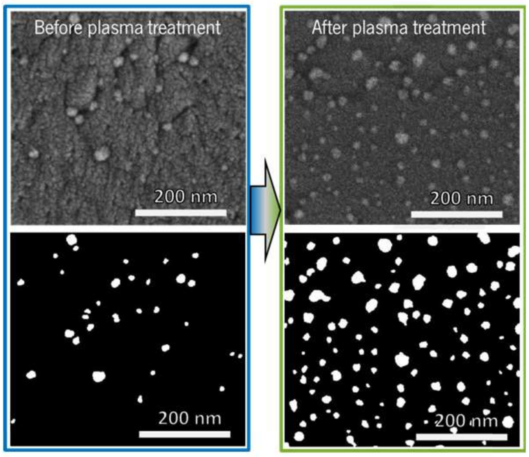
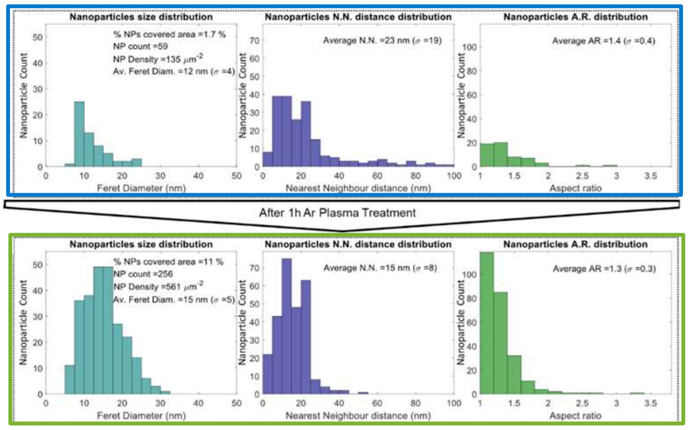
RESEARCH WORK

IMPROVING THE SENSITIVITY OF Au-TiO_2 THIN FILMS FOR OPTICAL GAS SENSING

Nanoparticle analysis

MATLAB Image processing to study nanoparticles' size and shape distribution





M.S. Rodrigues *et al,* Materials, 2020

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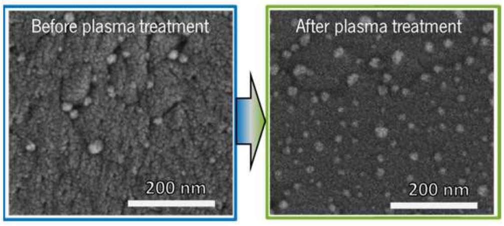
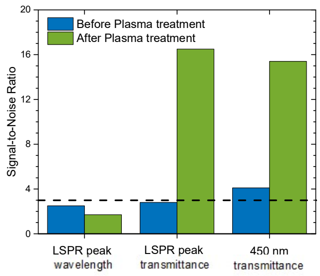
RESEARCH WORK

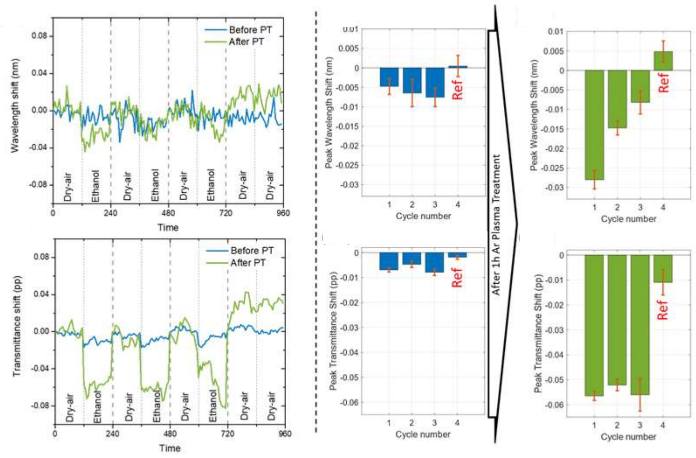
IMPROVING THE SENSITIVITY OF Au-TiO_2 THIN FILMS FOR OPTICAL GAS SENSING

T-LSPR monitoring – Ethanol sensitivity





Enhanced ethanol sensitivity after the partial exposure of Au nanoparticles



M.S. Rodrigues *et al*, Materials, 2020

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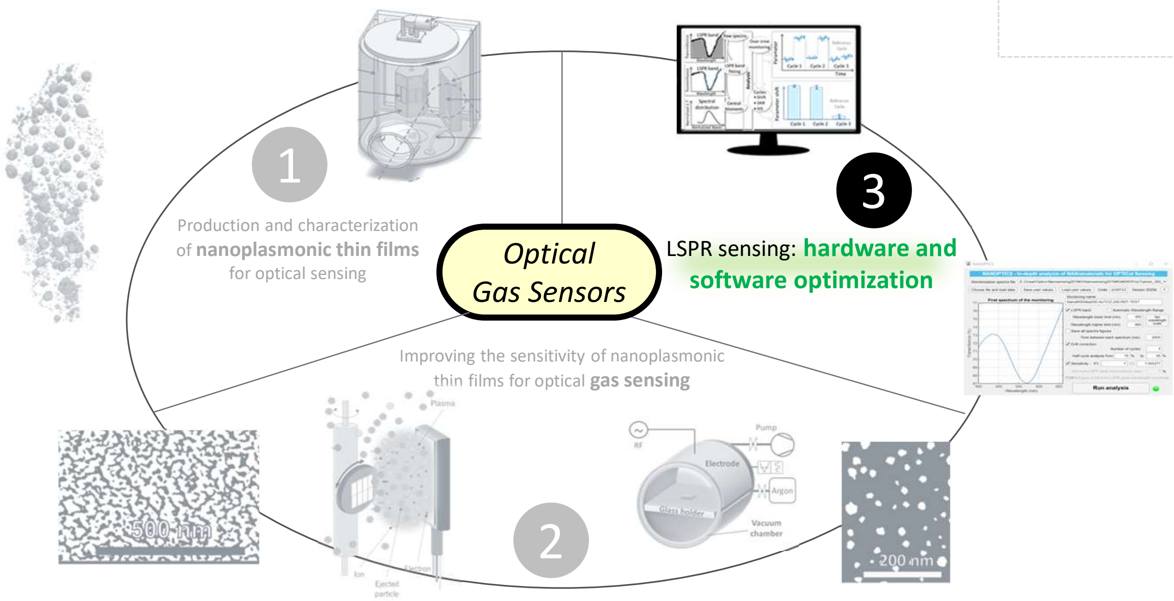
RESEARCH WORK

OBJECTIVES



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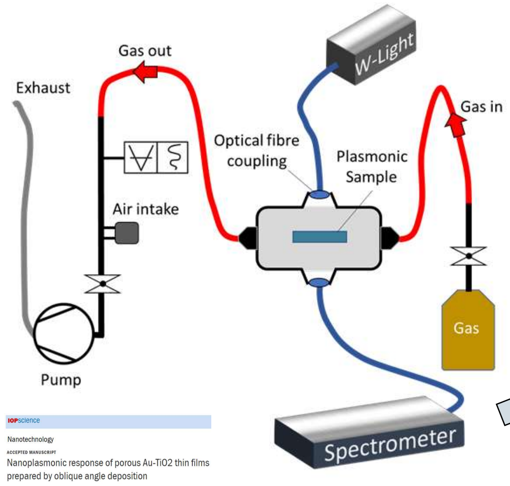
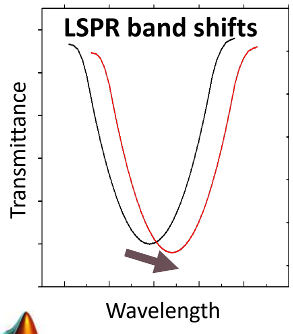
Optical gas sensing

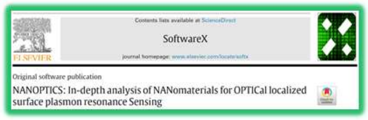


Hardware + Software



MATLAB signal processing

T-LSPR band analysis to detect gas presence



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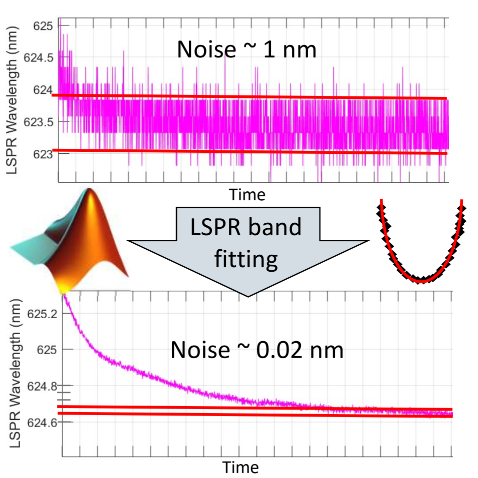
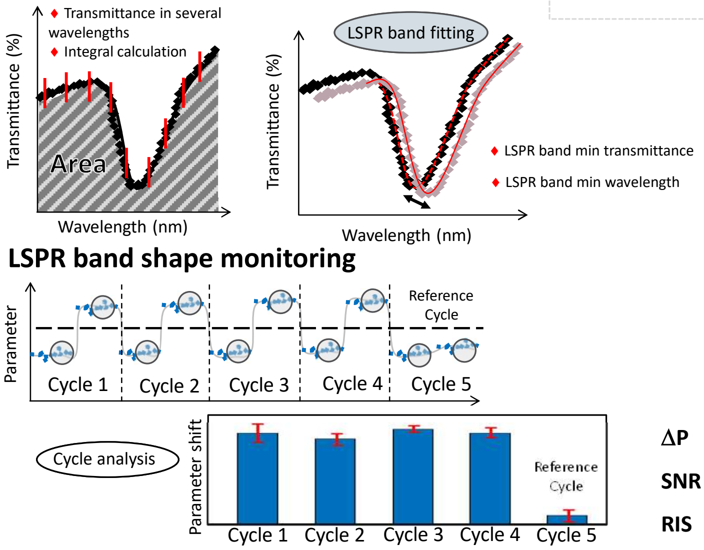
MATLAB LSPR sensing algorithm

LSPR Peak wavelength monitoring





ΔP

SNR

RIS

22

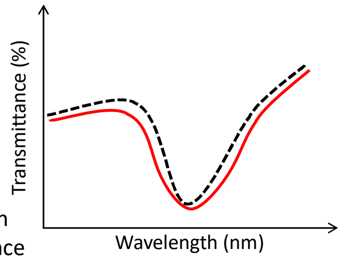
MATLAB LSPR Sensing algorithm

Raw Spectra

Parameters:
- ✓ Transmittance at discrete Wavelengths;
- ✓ Spectra Integral;
- ✓ Optical transmittance shift (OTC).

LSPR Band fitting

Parameters:
LSPR Peak:
- ✓ Wavelength
- ✓ Transmittance



Central Moments (Spectral Distribution)

$\lambda = \frac{\lambda'}{\lambda_{min}}$ Wavelength normalization

$M_0 = \int_{L1}^{L2} (1 - T(\lambda)) d\lambda$ (1-Transmittance) Integral

$P(\lambda) = (1 - T(\lambda))/M_0$ Normalized "Absorbance" spectral distribution

$M_1 = \int_{L1}^{L2} \lambda \, P(\lambda) \, d\lambda$ Expectation value

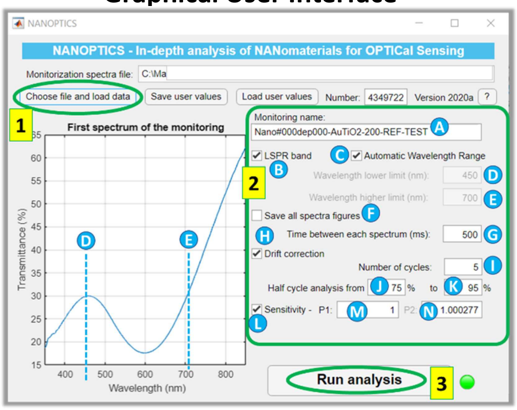
$M_2 = \int_{L1}^{L2} (\lambda - M_1)^2 \, P(\lambda) \, d\lambda$ Variance

$M_3 = \left(\int_{L1}^{L2} (\lambda - M_1)^3 \, P(\lambda) \, d\lambda \right) / ({M_2}^{3/2})$ Skewness (asymmetry)

$M_4 = \left(\int_{L1}^{L2} (\lambda - M_1)^4 \, P(\lambda) \, d\lambda \right) / ({M_2}^{2})$ Kurtosis (tail shape)

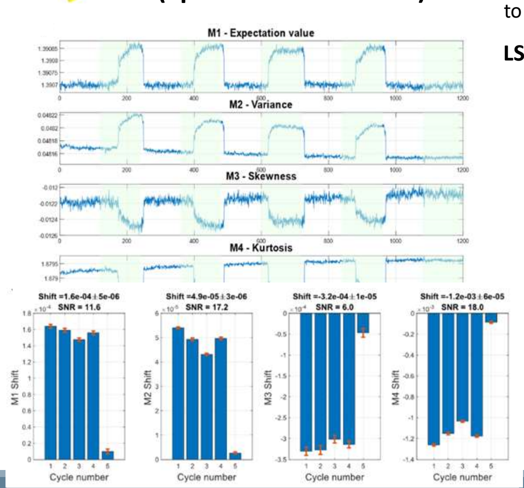
MATLAB LSPR Sensing algorithm

Graphical User Interface

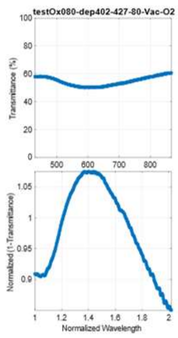


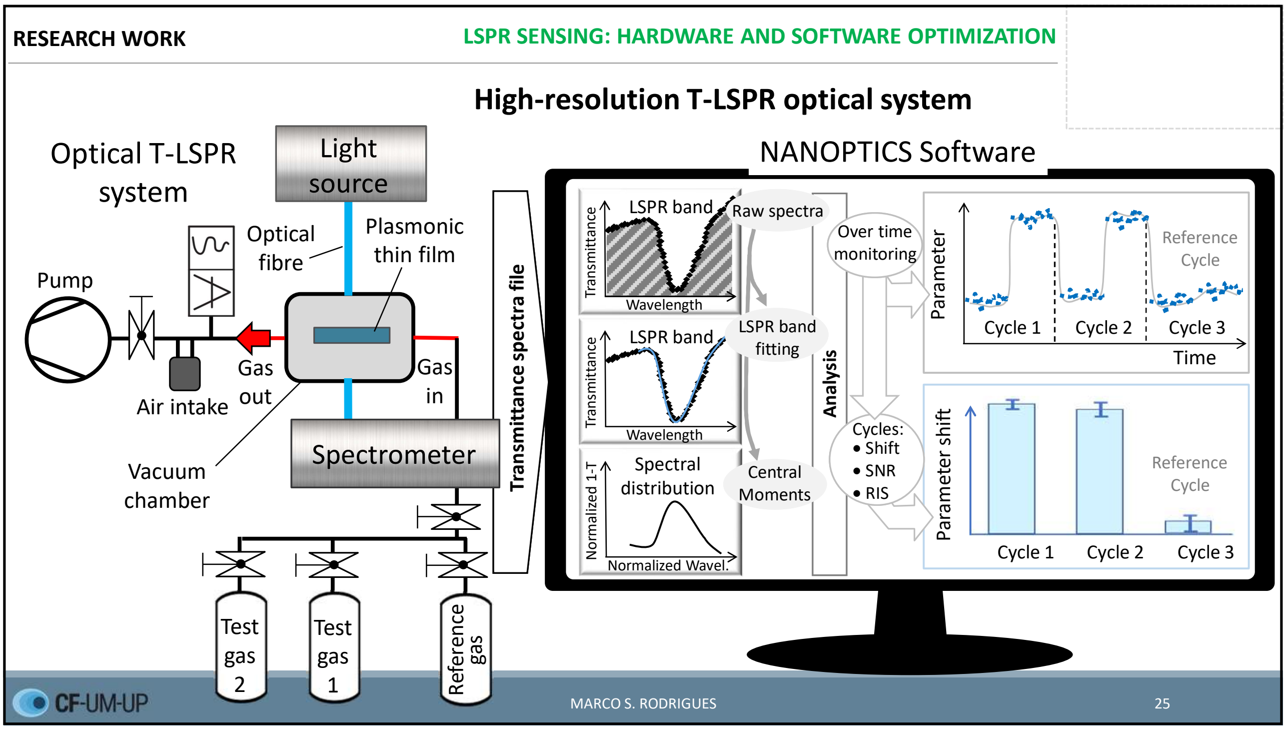
M.S. Rodrigues, *et al.*, Software X, 12 (2020), 100522

Central Moments (Spectral Distribution)



Normalized calculation to **compare different LSPR-based thin film sensors**




RESEARCH WORK
LSPR SENSING: HARDWARE AND SOFTWARE OPTIMIZATION
High-resolution T-LSPR optical system
Optical T-LSPR system
Light source
Optical fibre
Plasmonic thin film
Pump
Gas out
Gas in
Air intake
Vacuum chamber
Spectrometer
Test gas 2
Test gas 1
Reference gas
Transmittance spectra file
NANOPTICS Software
LSPR band
Raw spectra
Transmittance
Wavelength
LSPR band fitting
Spectral distribution
Central Moments
Normalized 1-T
Normalized Wavel.
Analysis
Over time monitoring
Cycles:
• Shift
• SNR
• RIS
Parameter
Cycle 1
Cycle 2
Cycle 3
Reference Cycle
Time
Parameter shift
CF-UM-UP
MARCO S. RODRIGUES
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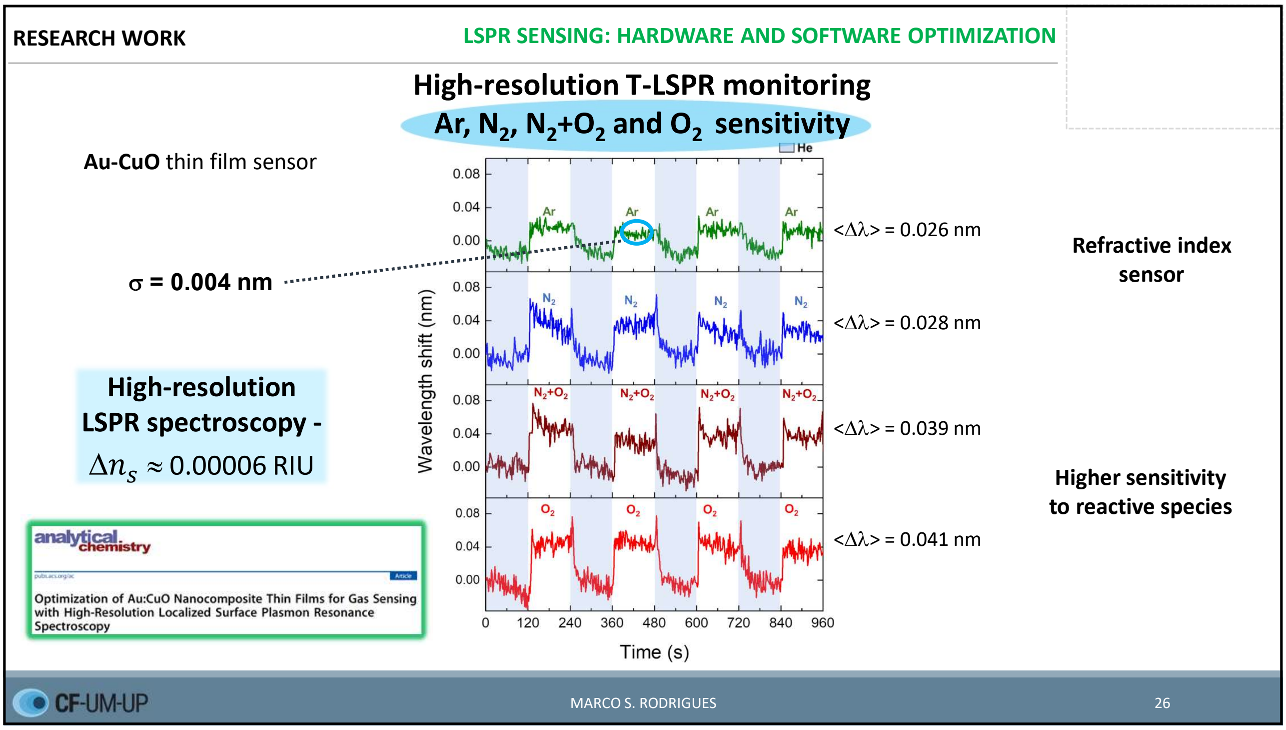
RESEARCH WORK
LSPR SENSING: HARDWARE AND SOFTWARE OPTIMIZATION
High-resolution T-LSPR monitoring
Ar, N$_2$, N$_2$+O$_2$ and O$_2$ sensitivity
Au-CuO thin film sensor
σ = 0.004 nm
High-resolution LSPR spectroscopy - $\Delta n_s \approx 0.00006$ RIU
analytical chemistry
Optimization of Au:CuO Nanocomposite Thin Films for Gas Sensing with High-Resolution Localized Surface Plasmon Resonance Spectroscopy
He
Ar
N$_2$
N$_2$+O$_2$
O$_2$
Wavelength shift (nm)
Time (s)
<Δλ> = 0.026 nm
<Δλ> = 0.028 nm
<Δλ> = 0.039 nm
<Δλ> = 0.041 nm
Refractive index sensor
Higher sensitivity to reactive species
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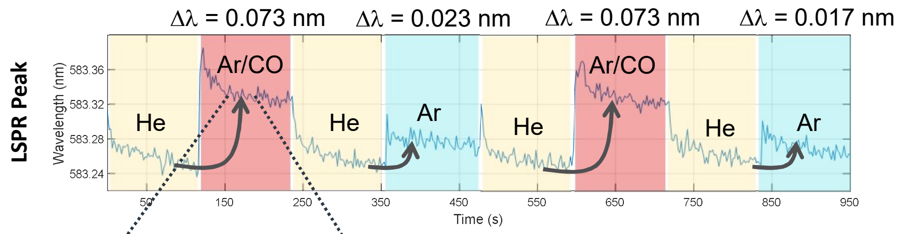
RESEARCH WORK

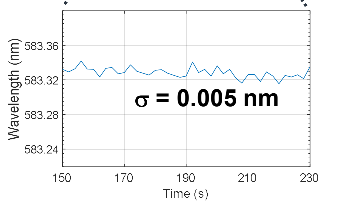
LSPR SENSING: HARDWARE AND SOFTWARE OPTIMIZATION

High-resolution T-LSPR monitoring

Carbon monoxide

Au-CuO thin film sensor





Refractive index sensor (He/Ar)

+

CO sensor
(50 ppm of CO in Ar)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Sensor integration

Carbon Monoxide (CO) Sensor Based on Au Nanoparticles Embedded in a CuO Matrix by HR-LSPR Spectroscopy at Room Temperature

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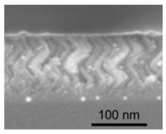
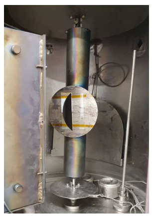
FINAL REMARKS

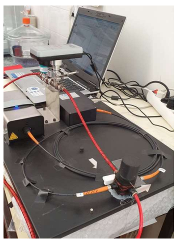
Future work

- ✓ Thin films with porous nanostructures exhibiting LSPR effect using other metal oxides/nitrides;
- ✓ Optical T-LSPR experiments for:
  - ✓ individual gases (CO_2, H_2) and gases in real-world conditions;
  - ✓ chemical and biological analytes in solutions;
  - ✓ physical properties (temperature, force, radiation)
- ✓ Integrate these sensors in a portable system

GLAD







Optical LSPR Spectroscopy for Gas Sensing

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THANK YOU FOR YOUR ATTENTION!

Nanostructured plasmonic thin films for LSPR sensing applications

25.09.21 MARCO S. RODRIGUES 29

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