

STUDY OF PLASMONIC NANOPARTICLES IN OXIDE THIN FILMS FOR SENSING APPLICATIONS

Inês Freitas^{1,2*}, Joel Borges³, Katharina Lorenz^{1,2,4,5} and Marco Peres^{1,2,4,5}

¹ Instituto Superior Técnico, Universidade de Lisboa, Portugal

² INESC MN, Lisbon, Portugal

*Corresponding author: MEFT (inesttfreitas@tecnico.ulisboa.pt)

³ Universidade do Minho, Braga, Portugal

⁴ IPFN, Instituto Superior Técnico, Universidade de Lisboa, Portugal

⁵ DECN, Instituto Superior Técnico, Universidade de Lisboa, Portugal

Motivation

ZnO is known for its wide bandgap and high exciton binding energy, and it is widely used in **sensors and transparent electronics**.

CuO, with its narrow bandgap and p-type behavior, is a promising candidate for visible light absorption and applications like **photovoltaics and gas sensing**.

Au nanoparticles (Au NPs) have distinct optical properties due to their ability to sustain **localized surface plasmon resonances (LSPR)**, which make them valuable candidates for applications in sensing, imaging, and energy harvesting. **Integrating these plasmonic nanoparticles into oxide thin films** allows for the combination of their functionalities, enhancing their performance.

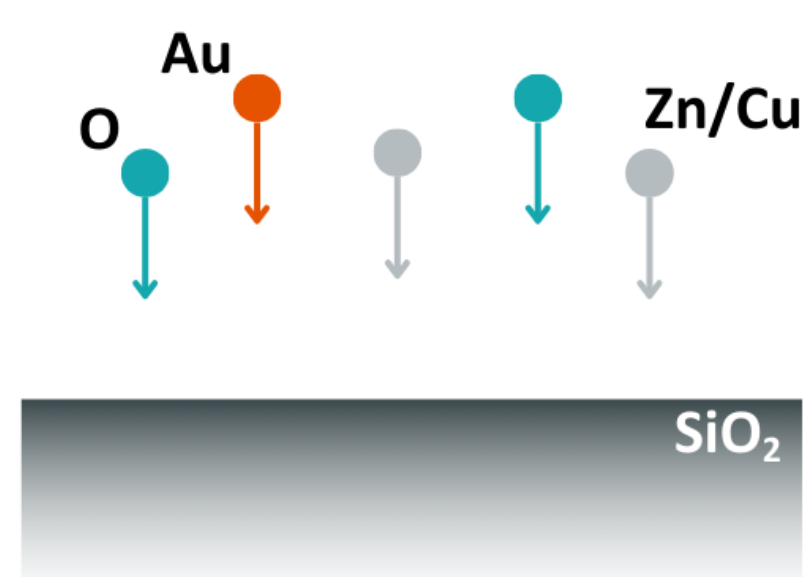
Ion implantation can be used as a NP formation method that offers **precise control over NP depth profile and concentration** by modulating the ion energy and implantation fluence. It is **ideal for multifunctioning devices** since it allows for the combination of different ions.

Objectives

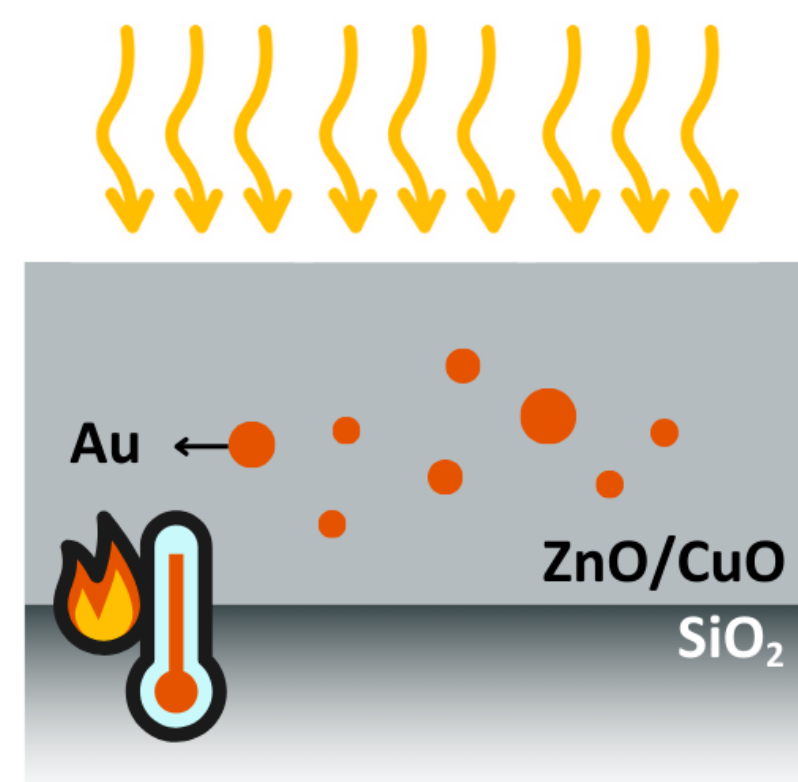
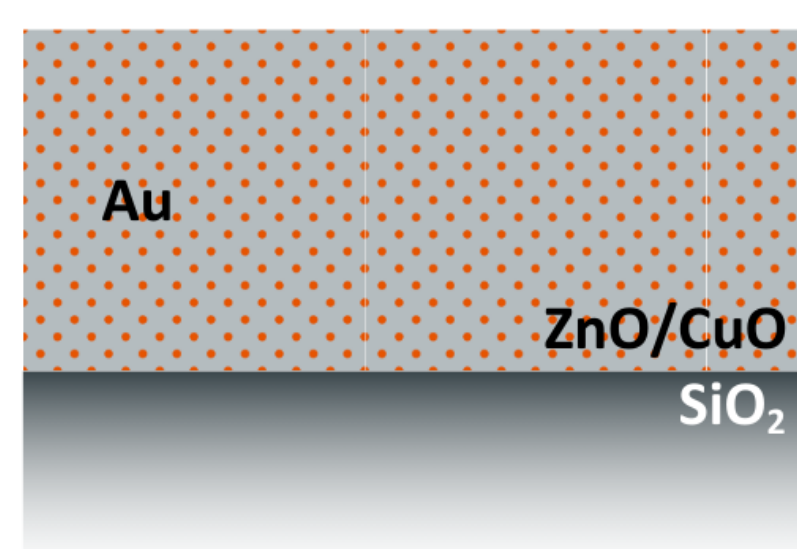
1. **Create Au NPs by ion implantation** in ZnO and CuO thin films;
2. **Compare two methods of NP formation:** *in situ* growth and ion implantation;
3. **Study the plasmonic temperature sensing potential** of Au-ZnO and Au-CuO composites.

Au NPs Formation

In situ growth



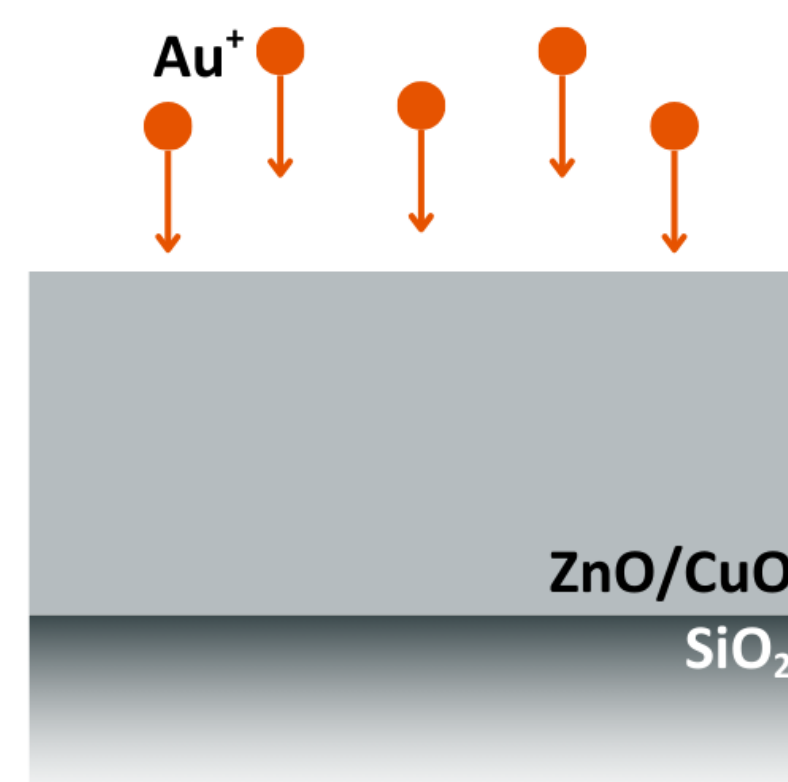
DC sputtering using oxide target + Au pellets



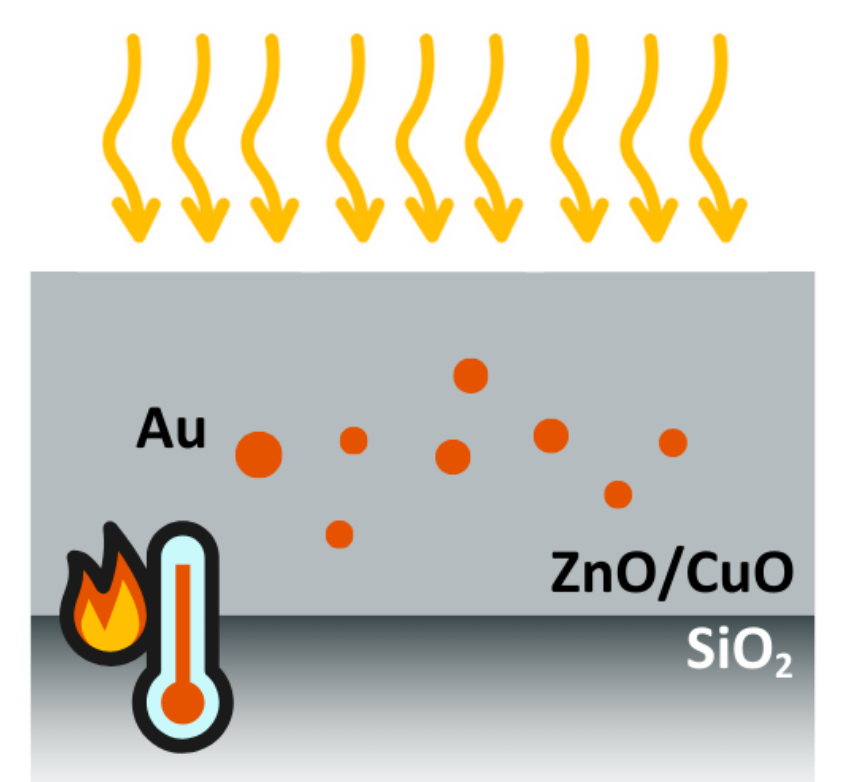
Thermal annealing in air
Temperature: 750 °C for ZnO and
800 °C for CuO

Offers uniform distribution of nanoparticles inside the film

Ion Implantation



DC sputtered oxide thin films are implanted with Au
Energy: 120 keV for ZnO and 150 keV for CuO
Fluence: 1×10^{16} ions/cm²



Thermal annealing in air
Temperature: 500 °C for ZnO and
700 °C for CuO

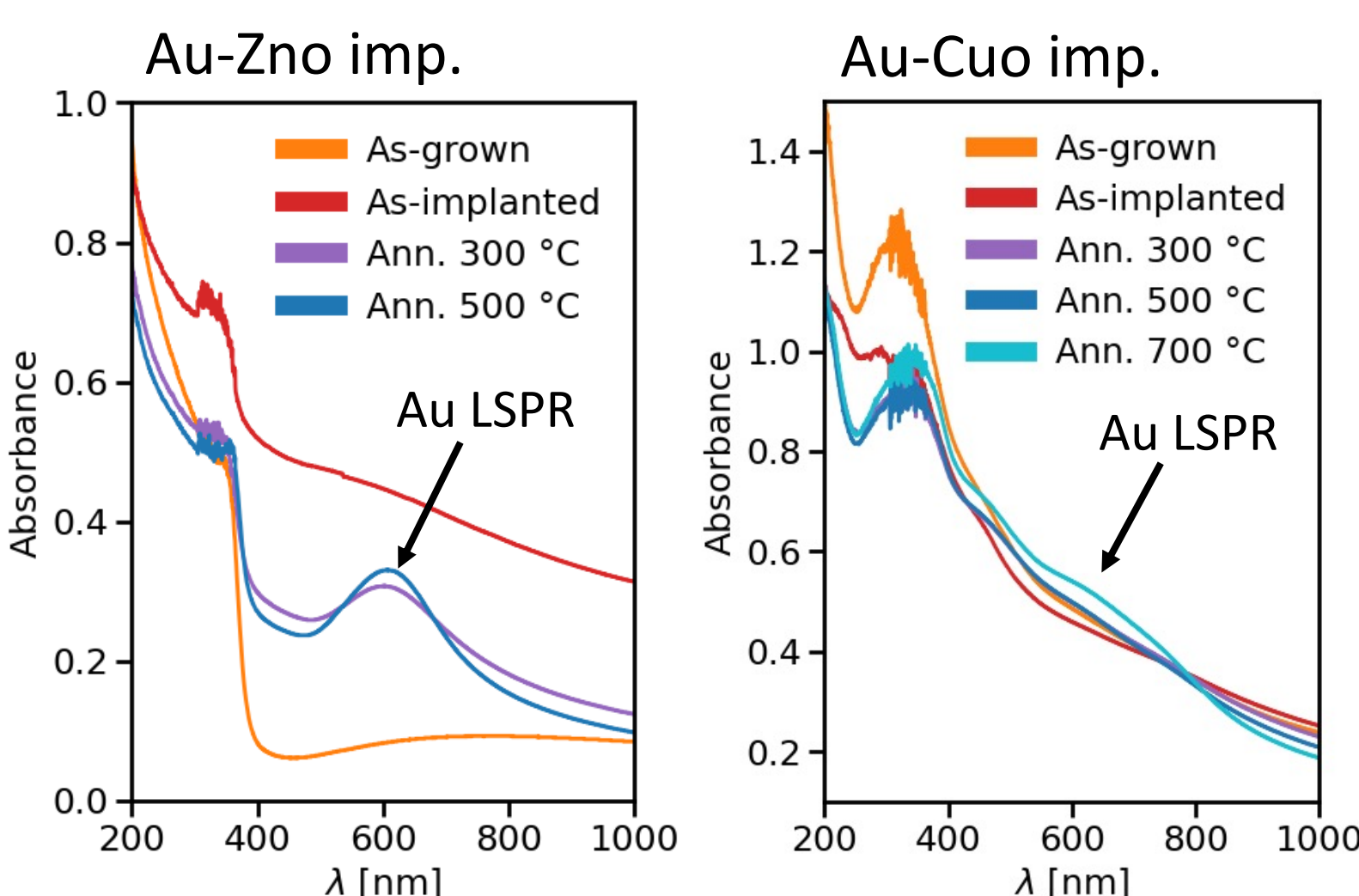
Offers precise control over nanoparticle depth profile

Characterization

Absorbance at RT

What are we looking for?

LSPR manifests as an absorption band in the spectra



LSPR absorption band becomes more defined with increasing annealing temperature in implanted samples

Why is LSPR stronger in *in situ* grown samples?

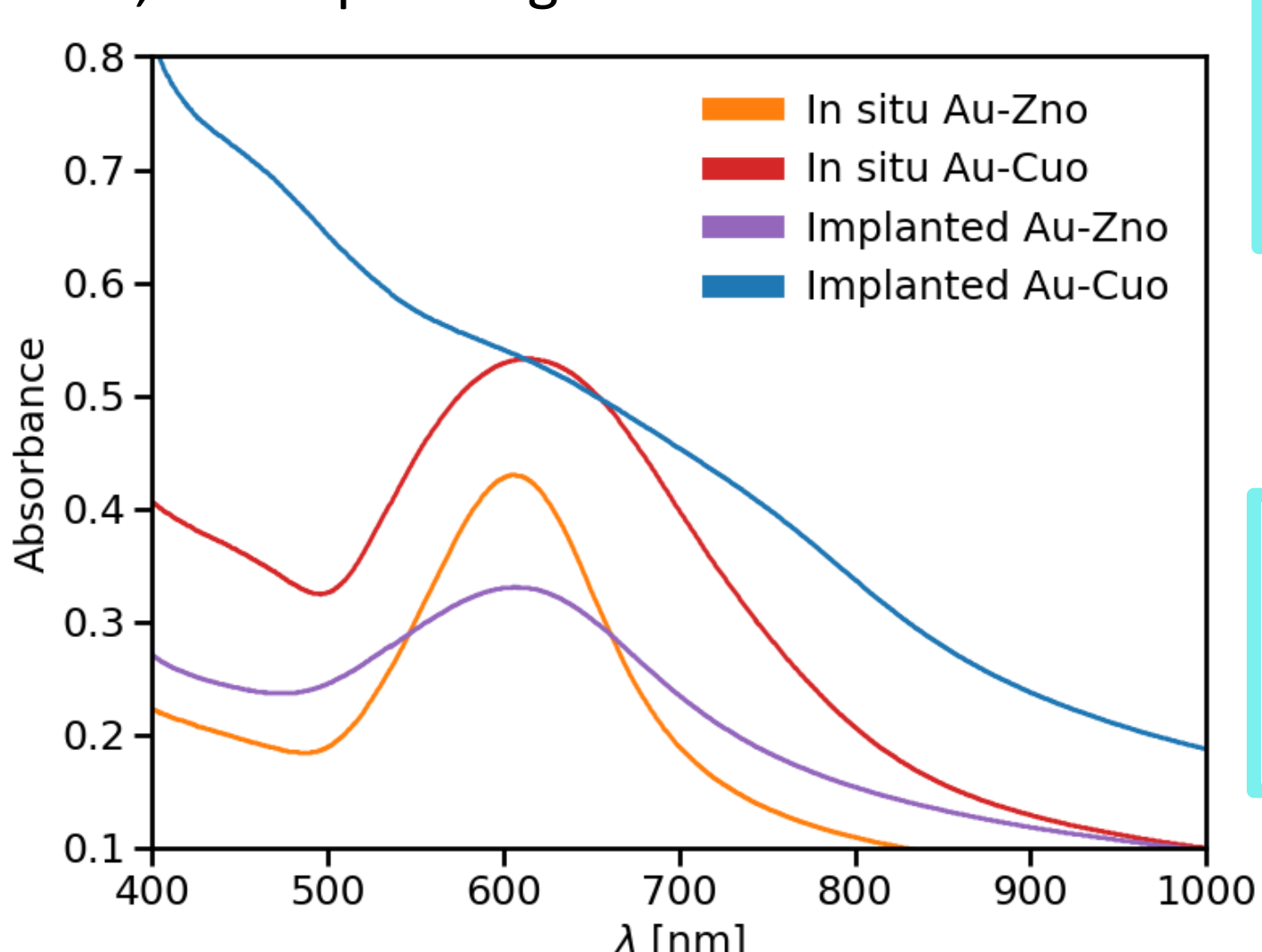
Higher Au amount
In situ: $\sim 5 \times 10^{16}$ ions/cm²
vs
Imp: $\sim 1 \times 10^{16}$ ions/cm²

Higher imp. fluences can sputter the thin film

Higher annealing T
In situ: 750 / 800 °C
vs
Imp: 500 / 700 °C

Higher annealing T can cause Au diffusion

The **absorption spectra** of the samples revealed an absorption band at **550–700 nm**, corresponding to the LSPR of **Au NPs**



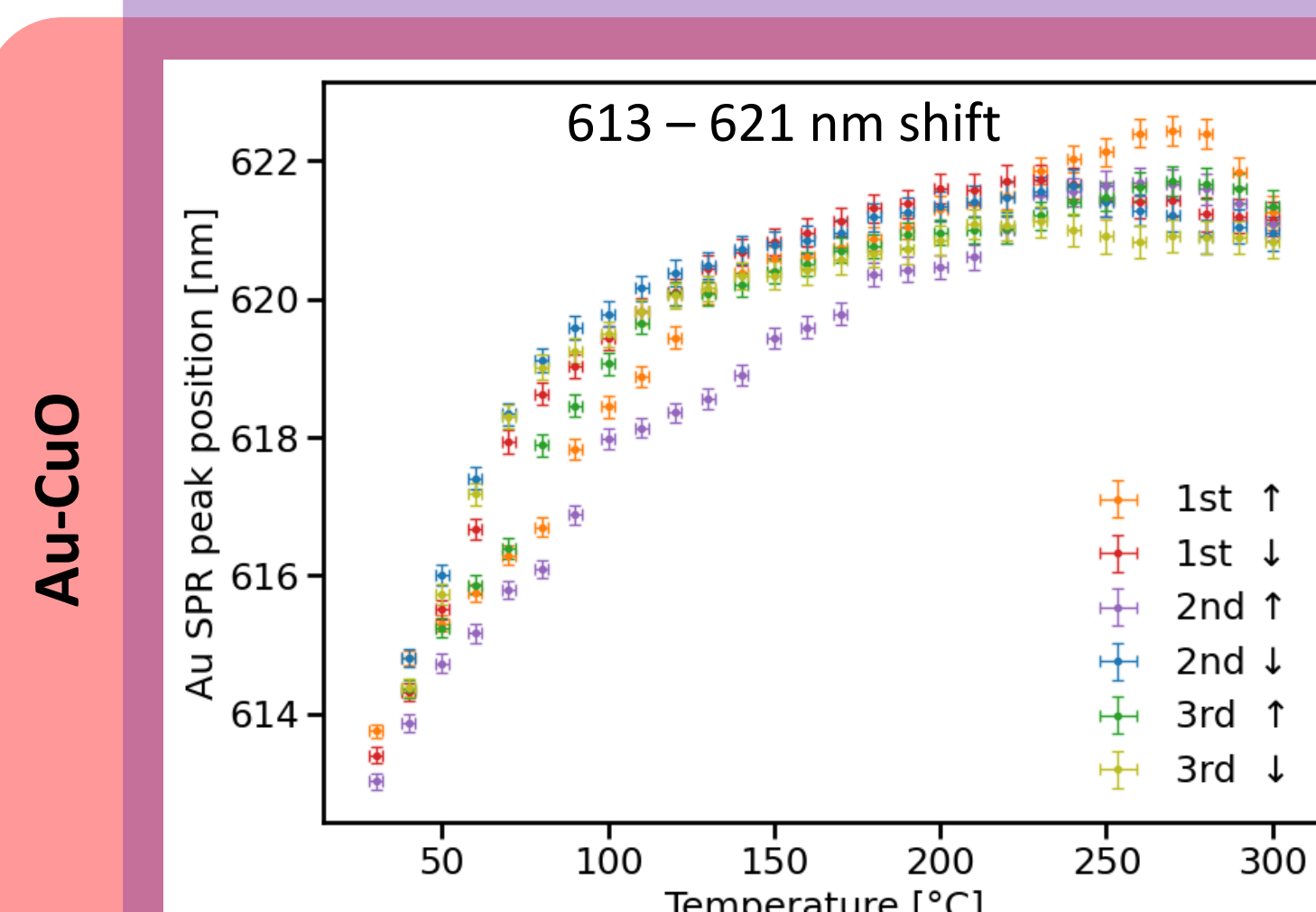
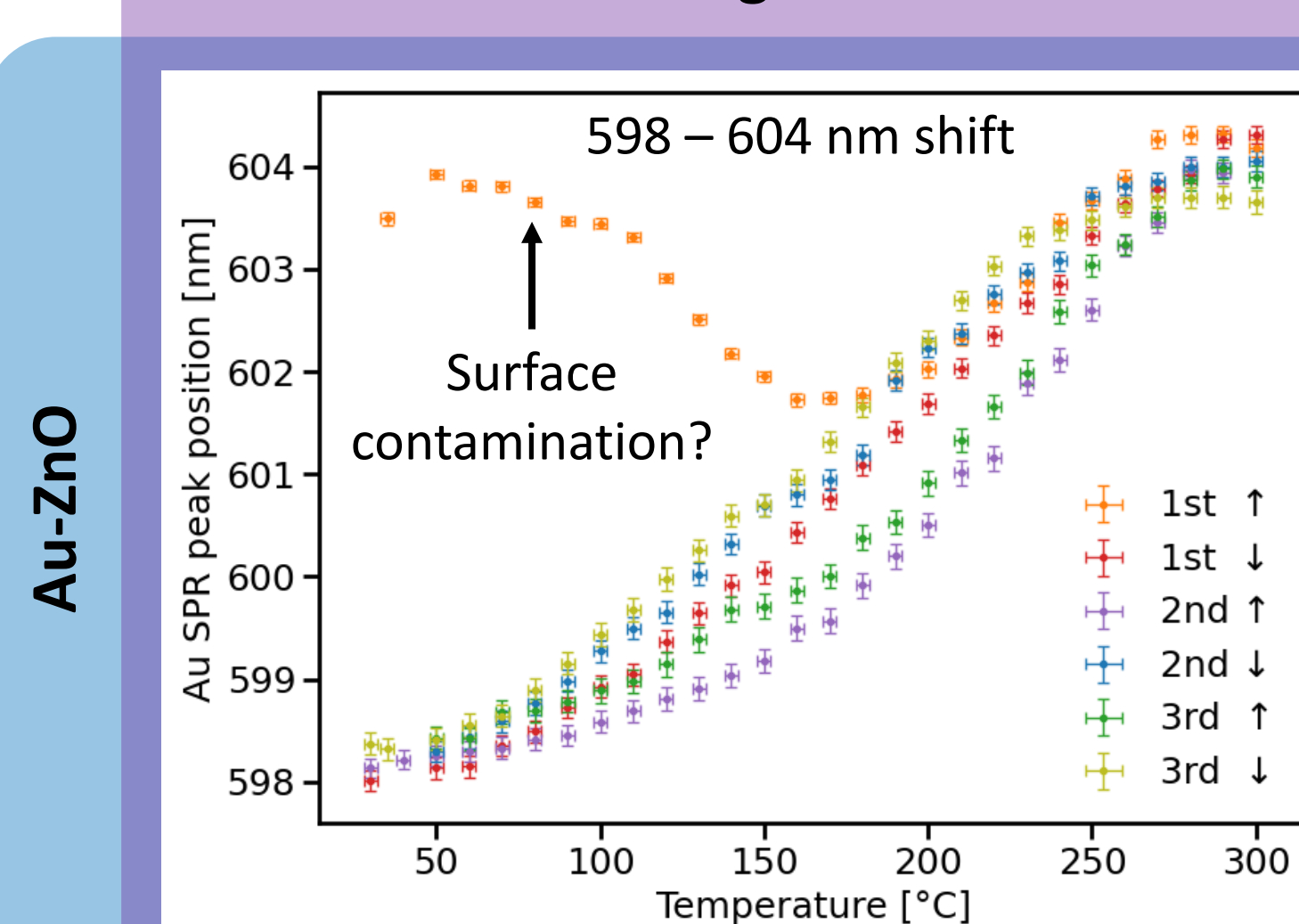
Results

Evaluation of Temperature Sensing Potential

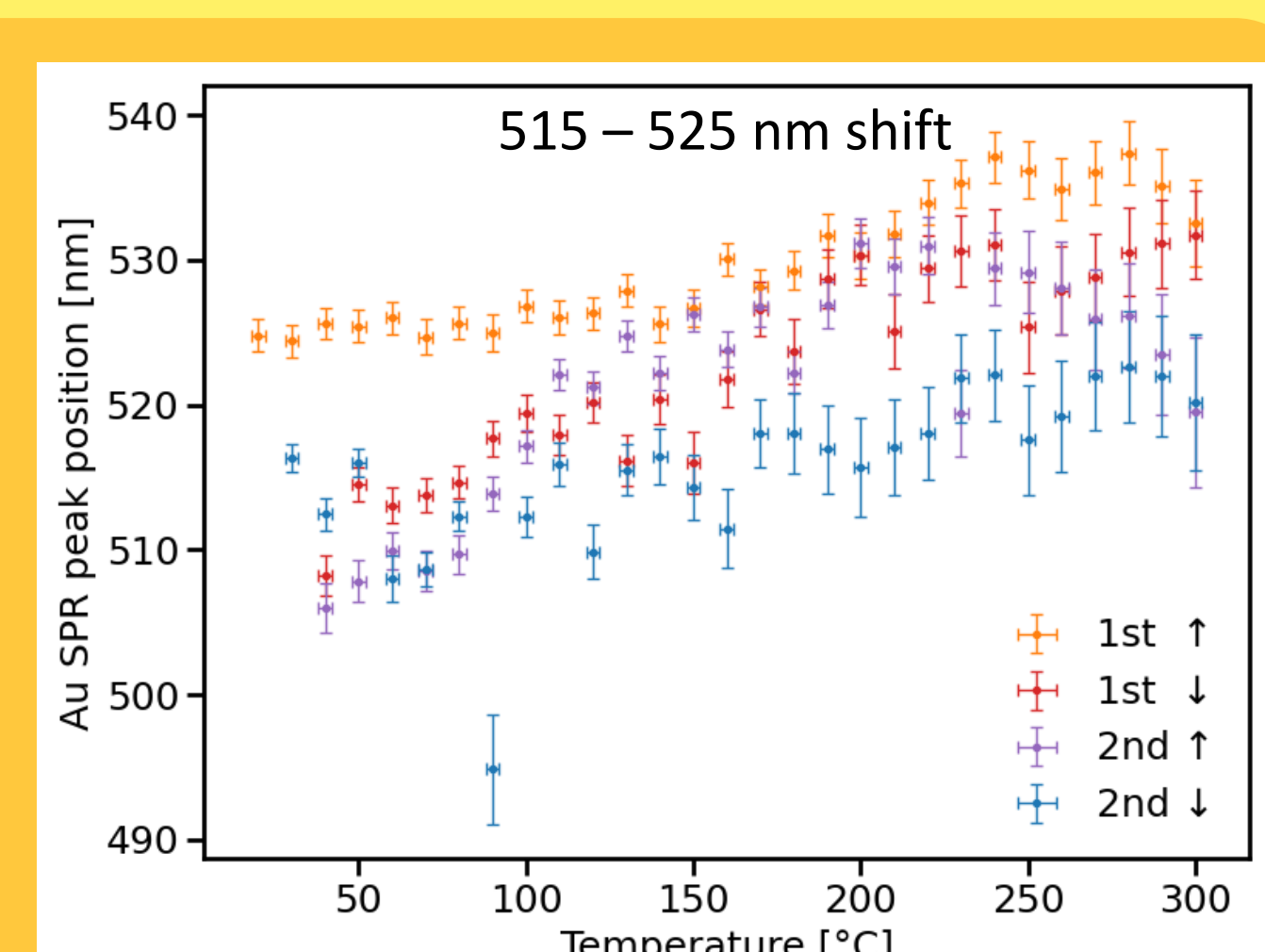
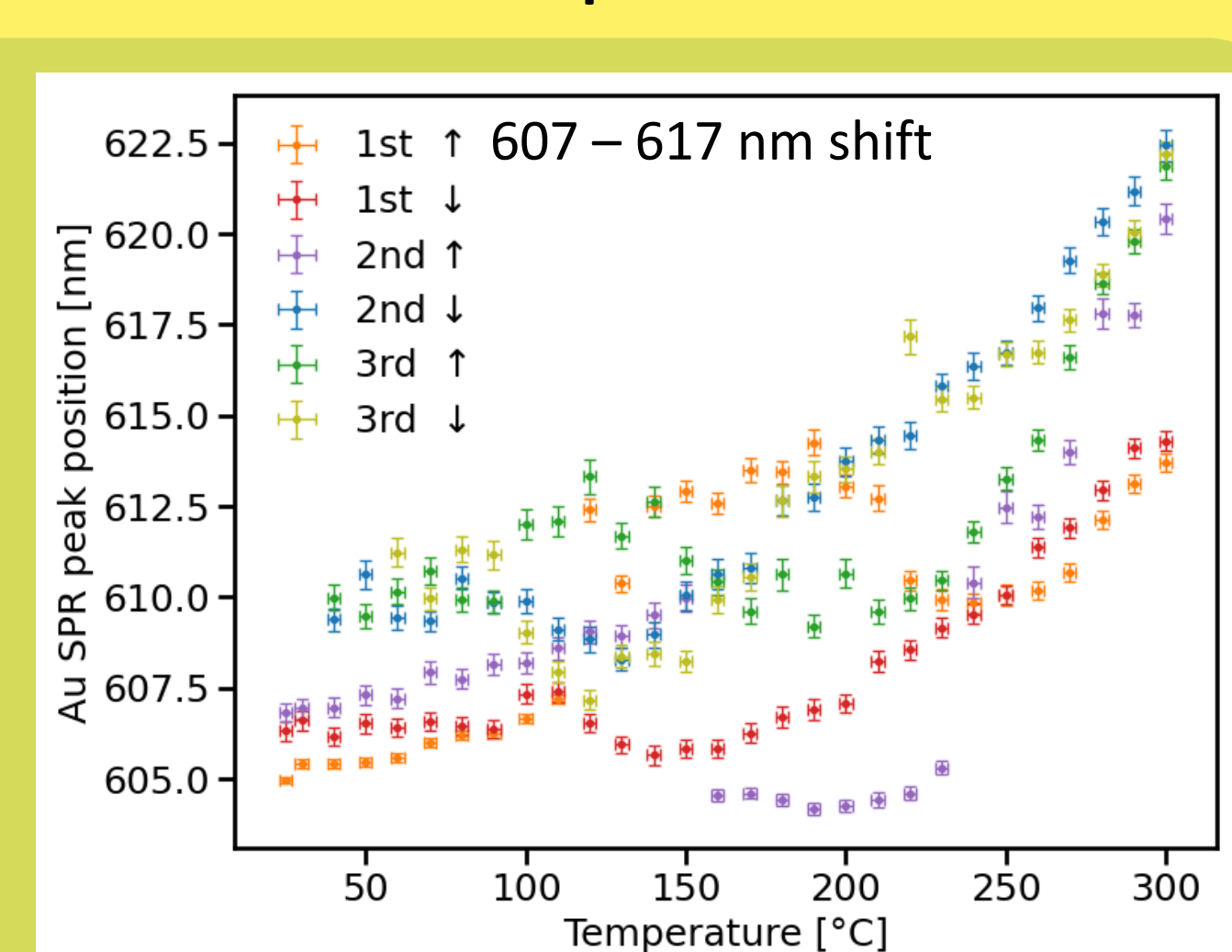
How was the study conducted?

1. Heated the samples from room temperature up to 300 °C
2. Measured the **optical transmission** while heating up (↑) and cooling down (↓) for multiple cycles
3. Analyzed the spectra by fitting gaussian on the absorption band range to obtain the LSPR peak position

In situ growth



Ion Implantation



Red-shift of the Au LSPR peak with increasing temperature

In agreement with the Drude model and Mie theory predictions

Shift attributed to electron–phonon scattering + thermal expansion of Au NPs + changes in the dielectric properties of the matrix

Possible **surface contamination** on *in situ* grown Au-ZnO deviates LSPR before the evaporation of adsorbed species!

Potential for **substance detection**

Conclusions

- Formed Au NPs in ZnO and CuO by ion implantation, enabling a comparison with the *in situ* growth method;
- Thermal annealing improved the plasmonic behaviour of the implanted samples, as the LSPR band became more defined;
- LSPR was stronger on *in situ* grown samples than on implanted samples, likely due to differences in Au quantity and thermal treatment;
- The LSPR absorbance band red-shifted with increasing temperature for all samples, which is in agreement with theoretical predictions;
- *In situ* grown Au-ZnO could be a candidate for substance detection, as possible surface contamination deviated the LSPR peak position.

All studied nanocomposites showed potential for temperature sensing

In situ grown Au-ZnO had the most linear LSPR peak shift

Future work

Experiment with higher implantation fluences and higher annealing temperatures for better comparison of NP formations methods

Acknowledgments

Research Unit INESC MN (UID/05367/2020) acknowledges FCT funding through pluriannual BASE and PROGRAMATICO. Financial support from project IonProGO (2022.05329.PTDC DOI: <https://doi.org/10.54499/2022.05329.PTDC>) and the EU Horizon Europe project ReMade@ARI are acknowledged.