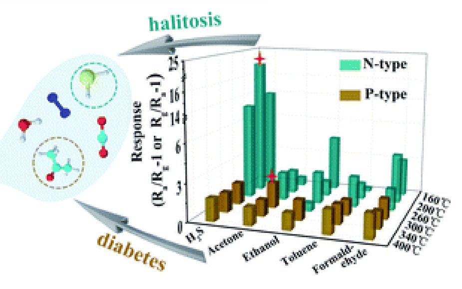
MatER Materials Science and Renewable Energies Group

Optoelectronic Properties of Al and Cr Co-Doped ZnO Bilayer Systems for Chemiresistive Gas Sensing of Volatile Organic Compounds

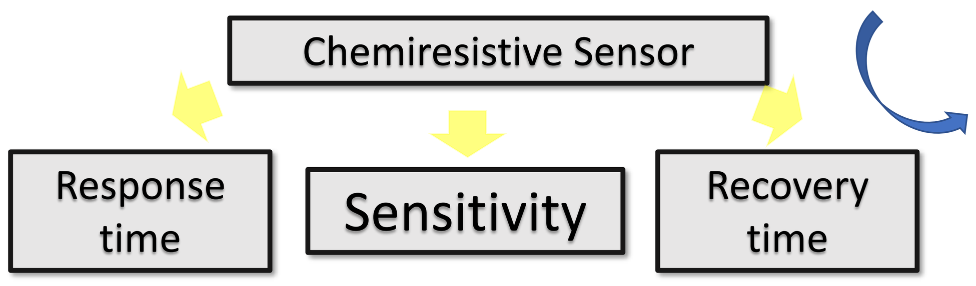
F. Bravo[1a], L. Sanchez[1], E. Serquen[1], J. Trevejo[2], L. Viera[1,2], L. Enrique[1], M. Sun-Kou[2] and J. A. Guerra[1b]

Introduction

Recently, gas sensors have emerged as a potential solution for non-invasive diagnosis of different diseases such as diabetes due to the excessive amount of ketone bodies generated in the breath due to insulin deficiency.



Sensor holder

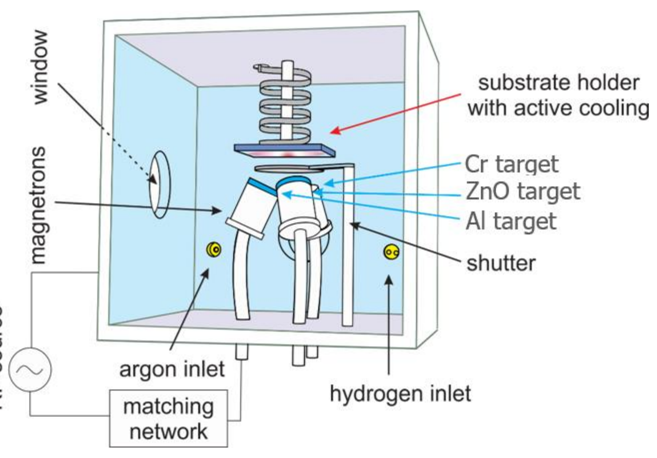


In this work, we analyze and contrast the structural and optoelectronic properties of Al doped ZnO (AZO) and Cr doped AZO prepared by RF Magnetron Sputtering and Sol-gel Spin-coating processes. A bilayer chemiresistive sensor based on Cr/Al co-doped ZnO (AZO:Cr), featuring a porous, lightly doped top layer (0.1 at % Cr) deposited by sol-gel spin-coating on a denser moderately doped bottom layer (1–4 at. % Cr) grown by RF magnetron sputtering.

Experimental details

Magnetron Sputtering

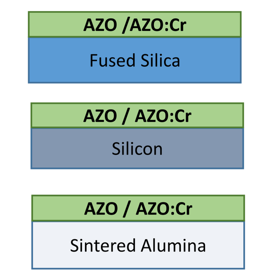
AZO and Cr doped AZO were deposited on fused silica, silicon and alumina substrates in an Ar atmosphere mixture using high purity AZO and Cr targets to obtain Al/Cr atomic ratio in the range of 0 to 5.



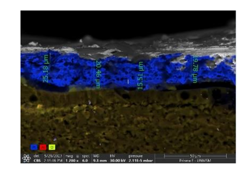
Conditions	Value
Power (W)	80 (AZO) 7-13 (Cr)
Deposition time (min)	60
Basic pressure (mbar)	2 x10^{-6}
Gas flux (sccm)	Ar (30)

Dopant concentrations and **post-annealing at 500 °C** (Ar atmosphere) engineer oxygen vacancies ($V_O^{\bullet\bullet}$), zinc interstitials ($Zn_i^{\bullet\bullet}$), and Cr^{3+} d-state levels, while Cr passivation of Zn vacancies (V_{Zn}''), enhances lattice thermal stability and enables carrier density modulation (~10^{19} – 10^{20} cm^{-3}) governed by Cr/Al ratio.

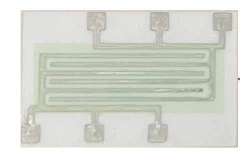
Stack Structure



Sensor Substrate



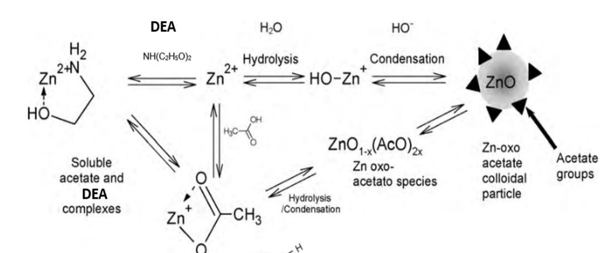
Annealed in Ar/500°C



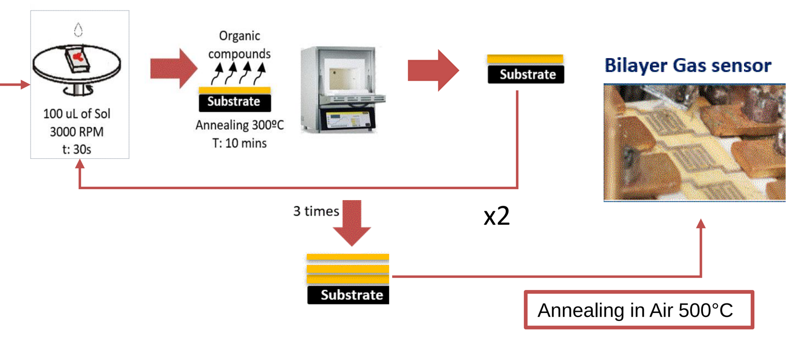
Sol gel Synthesis

Sol solutions were prepared employing ethanolamine as stabilizing and isopropanol as solvent. The precursors were Zinc acetate, Aluminum chloride and Chromium nitrate.

Conditions
Constant stirring at 60°C, for 2hrs at pH 6.



Spin Coating

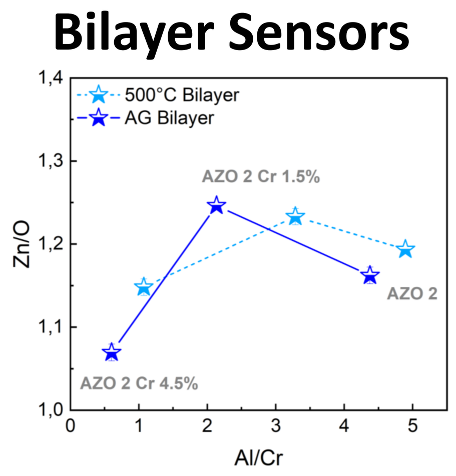


Results and discussion

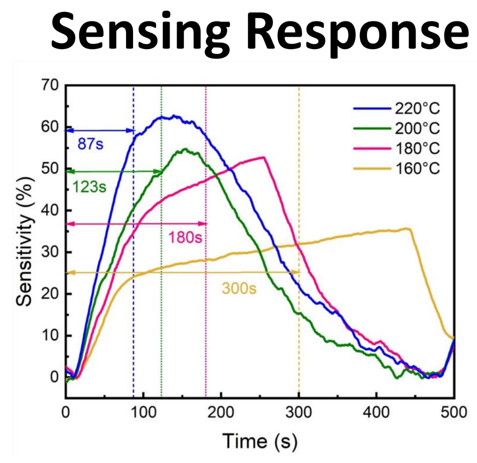
Gas Sensing Measurements

Changes in the sensor's resistances were monitored at different heating temperatures.

Bilayer Sensors

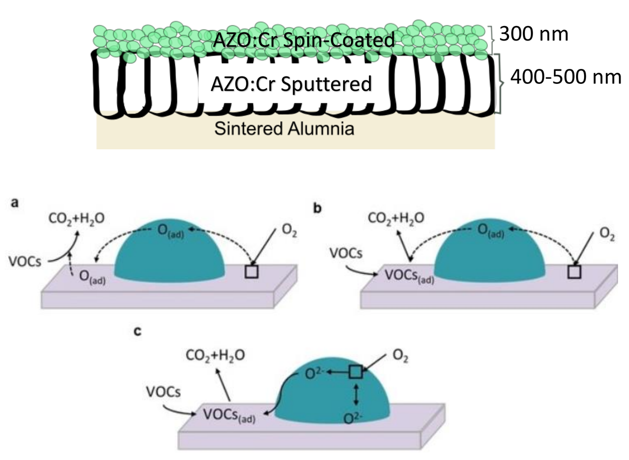


Sensing Response



Co-doped film-based AZO:Cr bilayer sensors showed superior performance due to enhanced adsorption-desorption kinetics. Optimizing the Al/Cr ratio is key to tuning defects composition, surface activity, and stability.

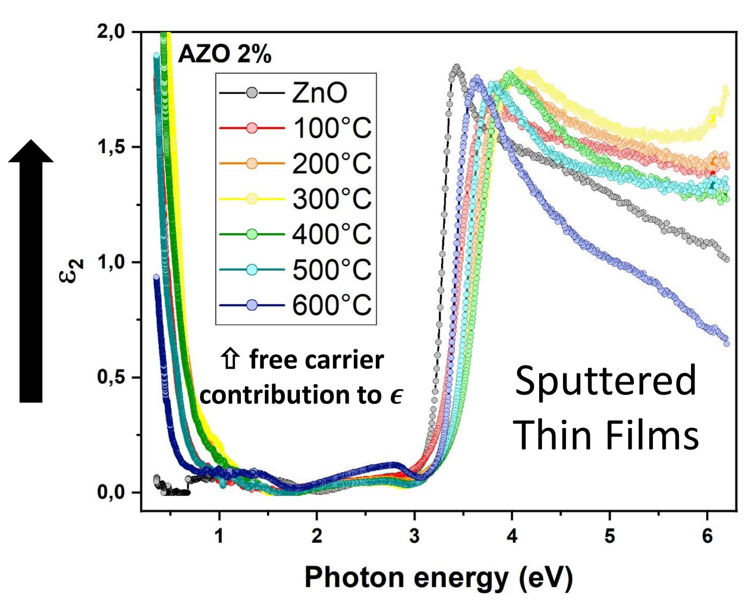
Sensing Mecanisms

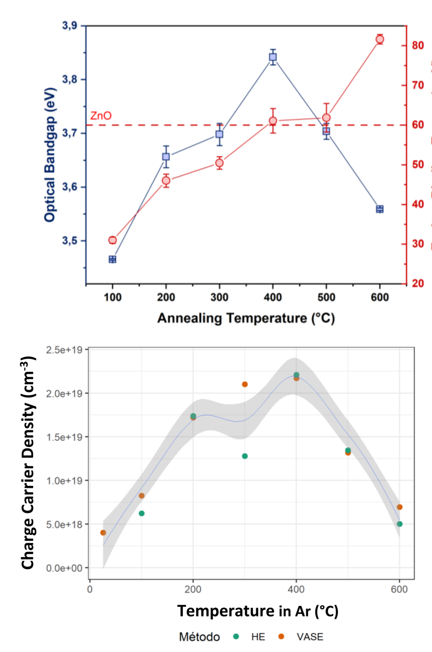


(a) Eley-Rideal (E-R)
(b) Langmuir-Hinshelwood
(c) Marse-van Krevelen

Variable Angle Spectroscopic Ellipsometry (VASE)

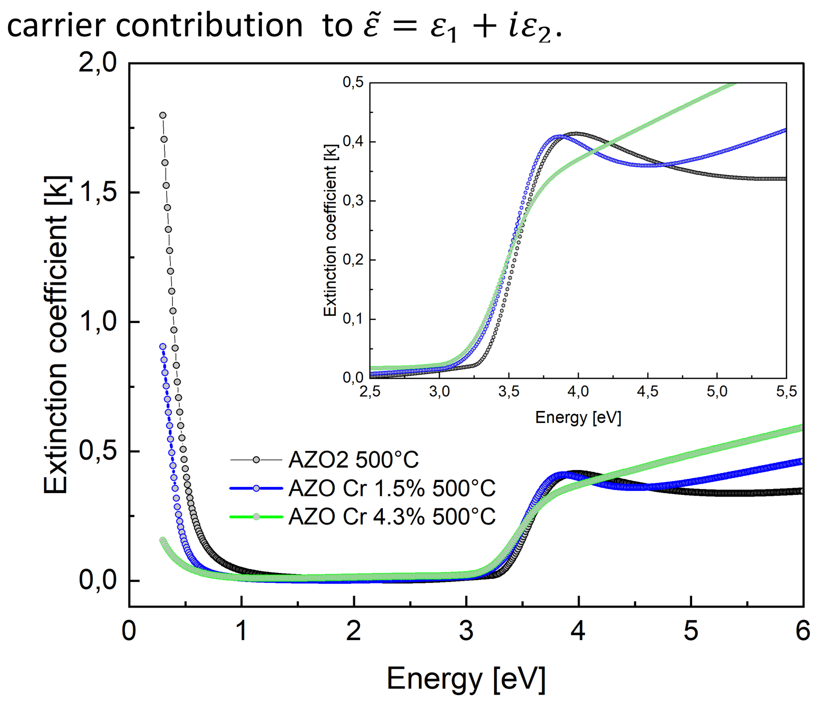
Fits to the complex part of the dielectric function ϵ_2 in the fundamental absorption region were performed to obtain the optical bandgap.



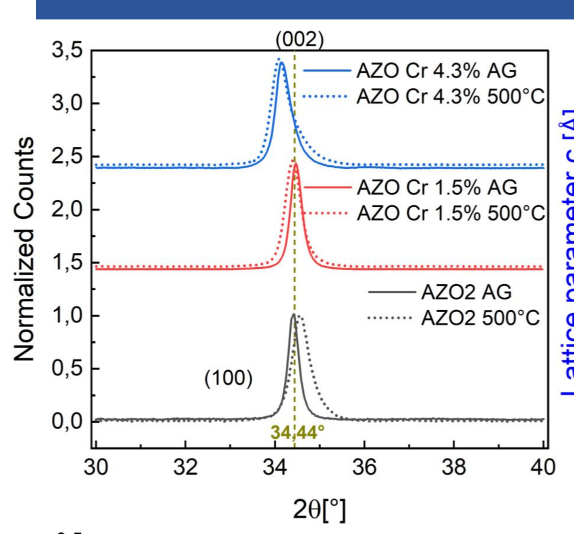


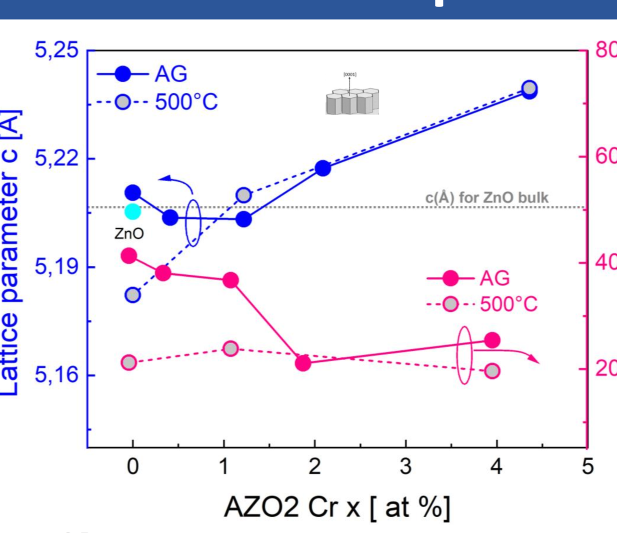
Optoelectronic Characterization

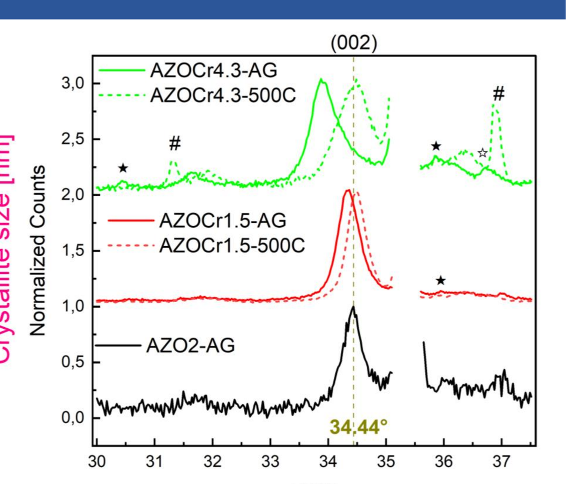
Drude Dispersion model was employed for the fitting the free carrier contribution to $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$.



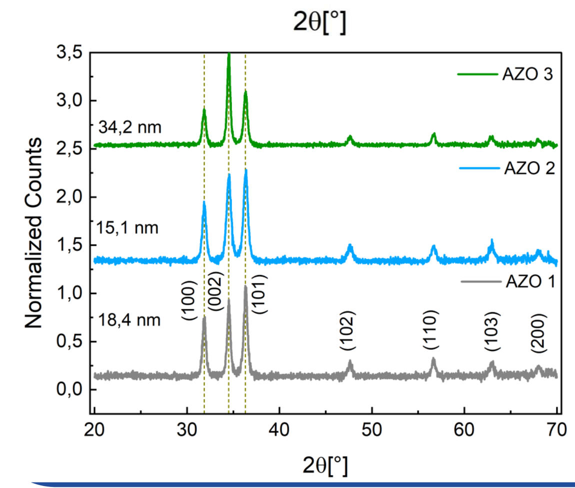
Structural Properties

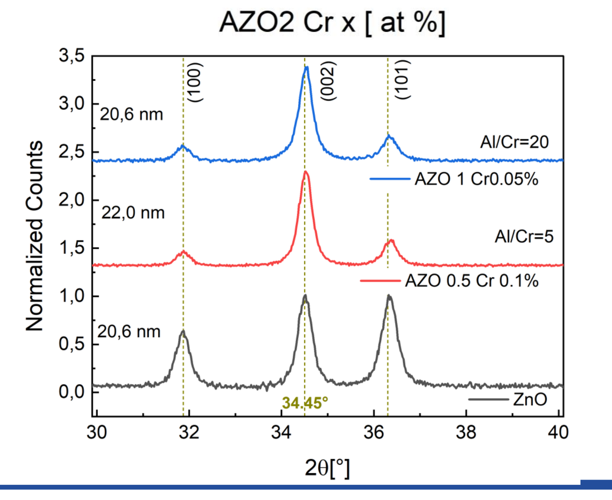






★: $ZnCr_2O_4$ ☆: $Cr_2O + Cr_2O_3$ #: $ZnAl_2O_4$

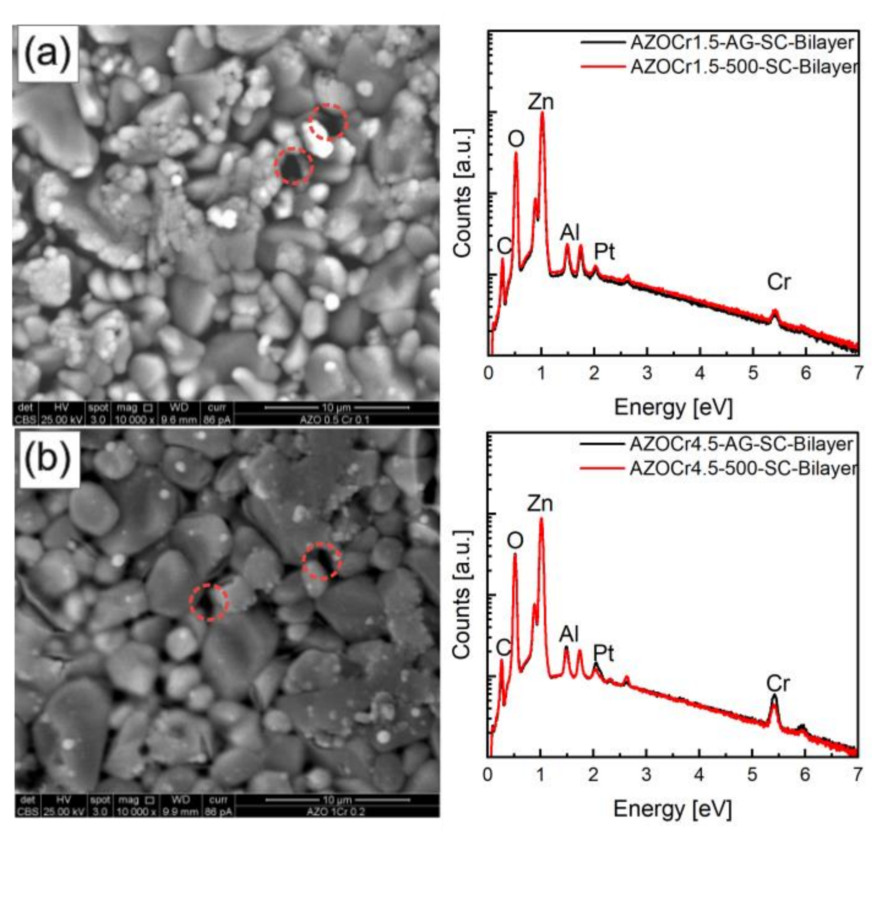




Sputtering thin films presented highly c-oriented wurtzite structures, this effect was also observed in spin coated thin films doped with Al and Cr.

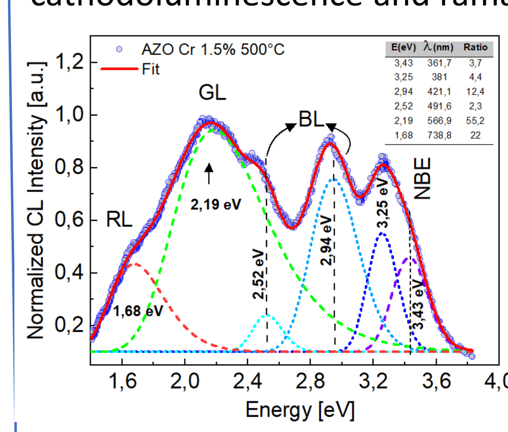
Secondary phases of Cr resulted in films with higher Cr content.

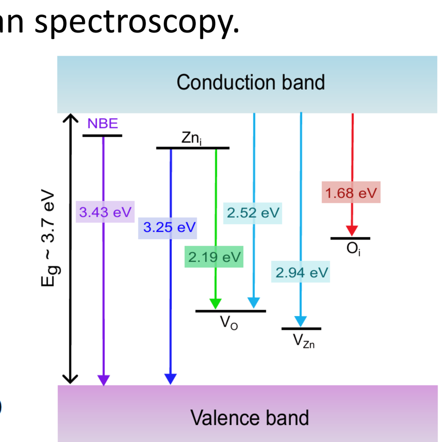
Morphological Properties

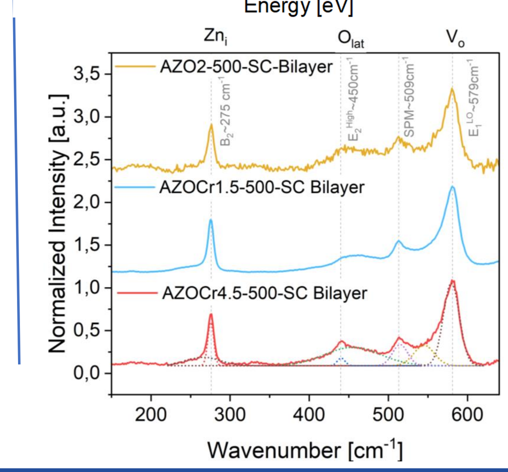


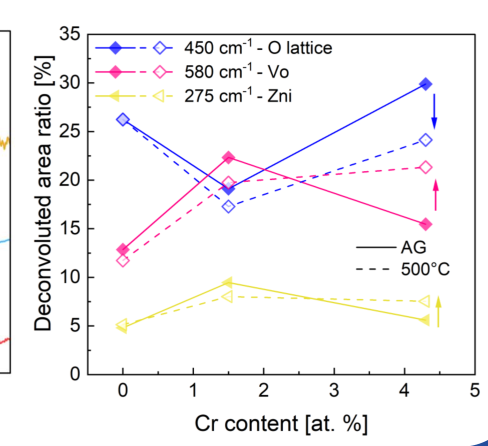
Defect Analysis

Zn_i and V_o defects have been identified through cathodoluminescence and raman spectroscopy.









Conclusions

- Engineered Cr/Al co-doping in ZnO bilayers (sputtered bottom: 1–4 at.% Cr/2 at.% Al; sol-gel top: 0.1 at.% Cr/1 at.% Al) modulates defects ($V_O^{\bullet\bullet}$ and $Zn_i^{\bullet\bullet}$) and carrier density (~10^{19}–$10^{20}$$cm^{-3}$), enhancing lattice stability via Cr passivation of Zn vacancies.
- Structural analyses of the bilayer sensing device revealed a highly c-oriented wurtzite (sputtered film) covered with a porous nanocrystalline network (15–30 nm). Spectroscopic analysis showed defect-induced sub-bandgap transitions, Burstein-Moss shift, and dielectric modulation, enabling >80% transmittance in transparent bilayer sensors.
- Gas sensing at 180–240 °C shows superior acetone response (>50% sensitivity at 0.1% V/V) via ionosorption/Eley-Rideal kinetics. Oxygen vacancies from spin-coated thin films doped with Cr could explain their improved sensitivity.

Next Steps

- Evaluate the photoactivation of bilayer sensors under different conditions.
- Perform electrical characterization of thin films under UV illumination.
- Evaluate bilayer sensors based of p-n heterojunctions.

Acknowledgments/References

ProCIENCIA N°179-202020-FONDECYT

[1] *J. Mater. Chem. A*, 2020,**8**, 26004-26012
[2] ***Chemical Physics Impact 2,*** 2021, 100019
[3] ***J. Phys. D: Appl. Phys.*** 2023, **56**, 365106
[4] ***Sensors** 2023, **23(13)***, 5864

Fondo Marco Polo
Office of Naval Research Science & Technology
CAP 2022 Concurso Anual de Proyectos de Innovación
CAMPUCP Centro de Caracterización de Materiales

1 Science Department, Physics Section, Pontifical Catholic University of Peru, Lima
2 Science Department, Chemistry Section, Pontifical Catholic University of Peru, Lima
[a] f.bravoh@pucp.edu.pe, [b] guerra.jorgea@pucp.edu.pe

PUCP