Crystalline transitions and point defects in (N, Mg)-doped copper oxide thin films deposited by RF magnetron sputtering

T. Ratz[1], E. Fourneau[2], N. Sliti[1], C. Malherbe[3], A. Baret[1], B. Vertruyen[4], A. V. Silhanek[2], N. D. Nguyen[1]

[1] SPIN, [2] EPNM - Department of Physics, [3] MOLSYS, [4] GREENMAT - Department of Chemistry
University of Liège, Belgium

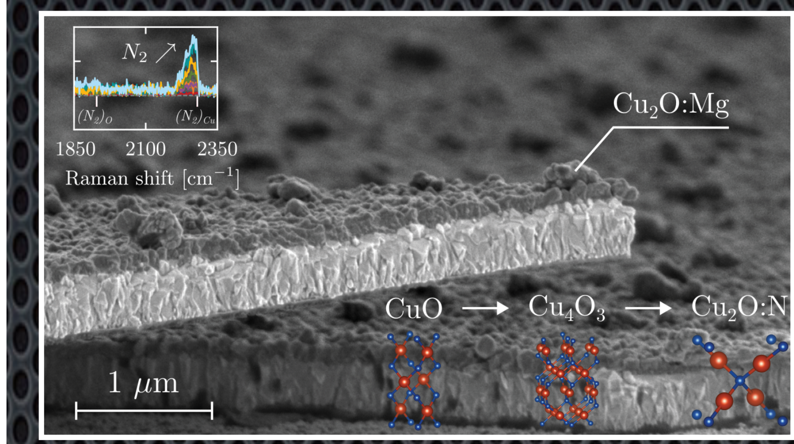
Context and motivation

Cu_2O is a promising transparent conducting oxide (TCO) for photovoltaic (PV) applications, with a large absorption coefficient on the order of 10^4 cm^{-1} and p-type conductivity with charge carrier concentration on the order of 10^{14} to 10^{17} cm^{-3}. Additionally, this material is abundant and nontoxic and can be synthesized using various chemical and physical routes.[1,2] The Shockley–Queisser (SQ) efficiency limit of Cu_2O-based solar cells is 20.5%, considering a 2.1 eV band gap as experimentally measured by Jolk *et al.* via excitonic absorption.[3-5]

Over the past 20 years, the efficiency of copper oxide based solar cells notably increased from 2% to the current world record of 8.4%, reported by Shibasaki *et al.* in 2021.[5-7] However, there remains a significant margin for improvement concerning the PV performance of this earth-abundant material.[7] Despite recent improvements, the efficiency is still limited by the open- circuit voltage and the fill factor values.[6-14] The former results from charge recombination processes in the bulk and at the interfaces, while the latter is partially associated with the poor electrical performances of the copper oxide absorber layer.[1,2,15] In order to circumvent these limitations, a deeper understanding of the microscopic mechanisms ruling the material's conductivity and its link to point defects is needed. In addition, as widely reported in recent years, material doping offers an interesting strategy first to inhibit the presence of defects acting as recombination centers and, second, to boost the material opto-electrical properties.

The objective of this work is to extend the scientific community's understanding of the role of point defects in intentionally doped copper oxide thin films. Additionally, we aim to further enhance the material opto-electrical performance via doping with N and Mg, as well as via (N,Mg) co-doping, appear as suitable elements in the case of copper oxide.[16-21]

T. Ratz *et al.*, *ACS Appl. Electron. Mater.* **7** (2), 643–651 (2025)   *Check our full paper online !*



2-inch targets : CuO (0Mg) and Cu_2O:Mg (4Mg)
Ar plasma (power 70 W, pressure 5 mTorr, flow 20 sccm)
No substrate heating, dopant flow : N_2 [0; 20] ccm

Materials and methodology

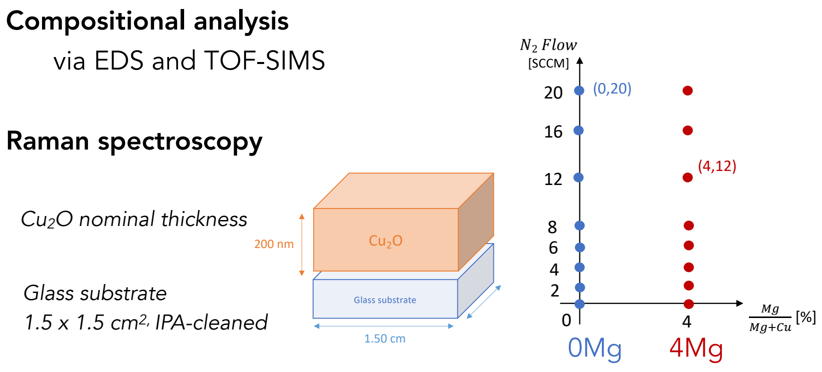
Thin film deposition by RF magnetron sputtering
Angstrom Engineering NEXDEP system

Optical and electrical characterizations
Shimadzu UV-Vis 3600 Spectrophotometer
PhysTech RH 2035 Hall effect measurement system

Morphological/elemental and structural characterizations
TESCAN Vega 3 scanning electron microscope (SEM/EDS)
Bruker Twin-Twin diffractometer with Cu Kα source

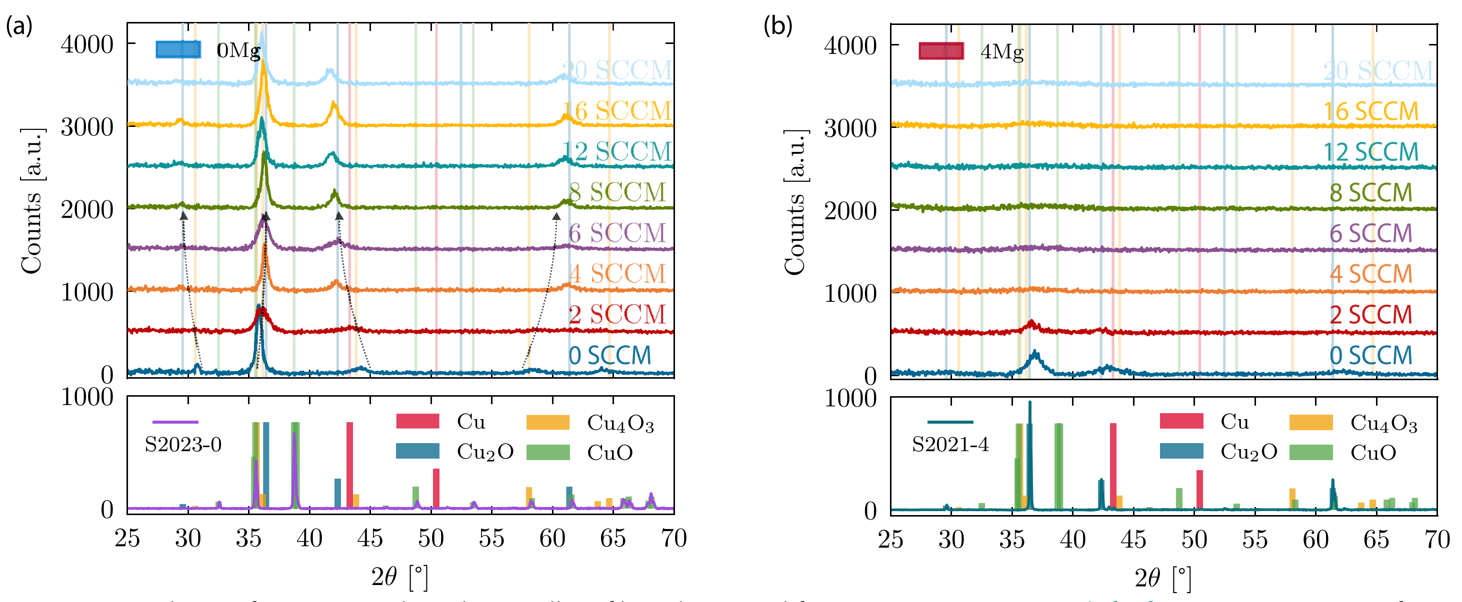
Compositional analysis
via EDS and TOF-SIMS

Raman spectroscopy



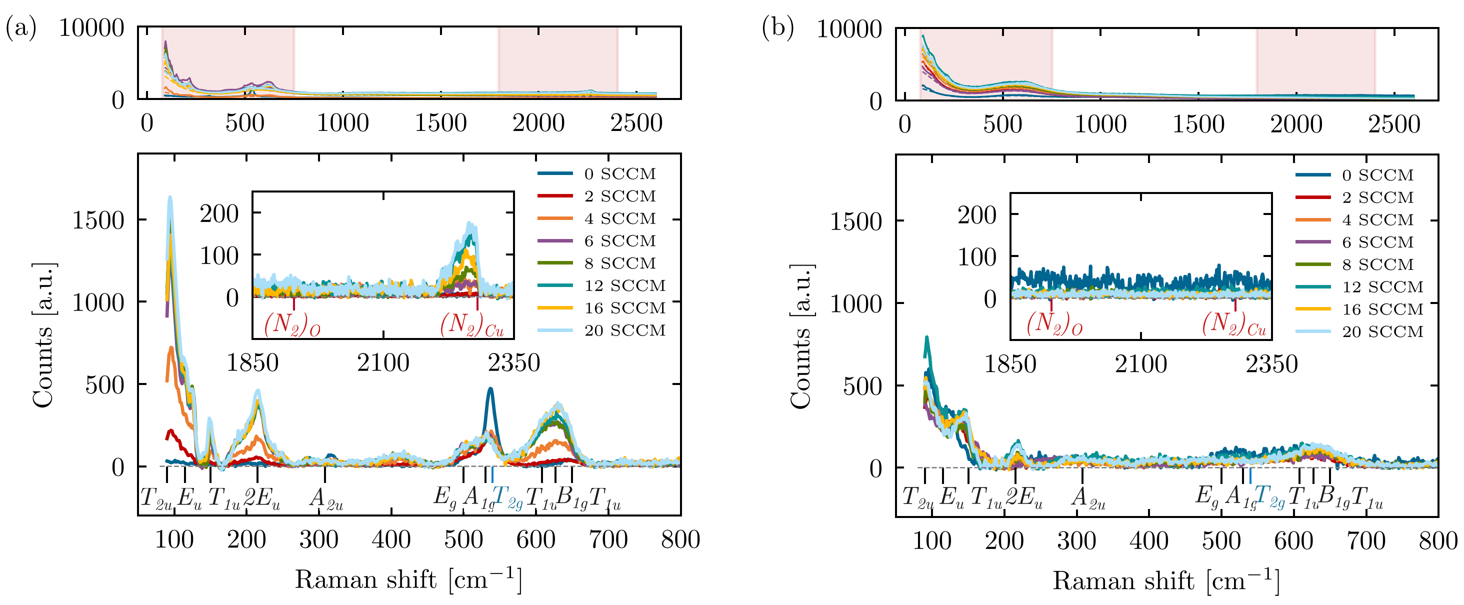
Measurements and results

X-ray diffraction spectra

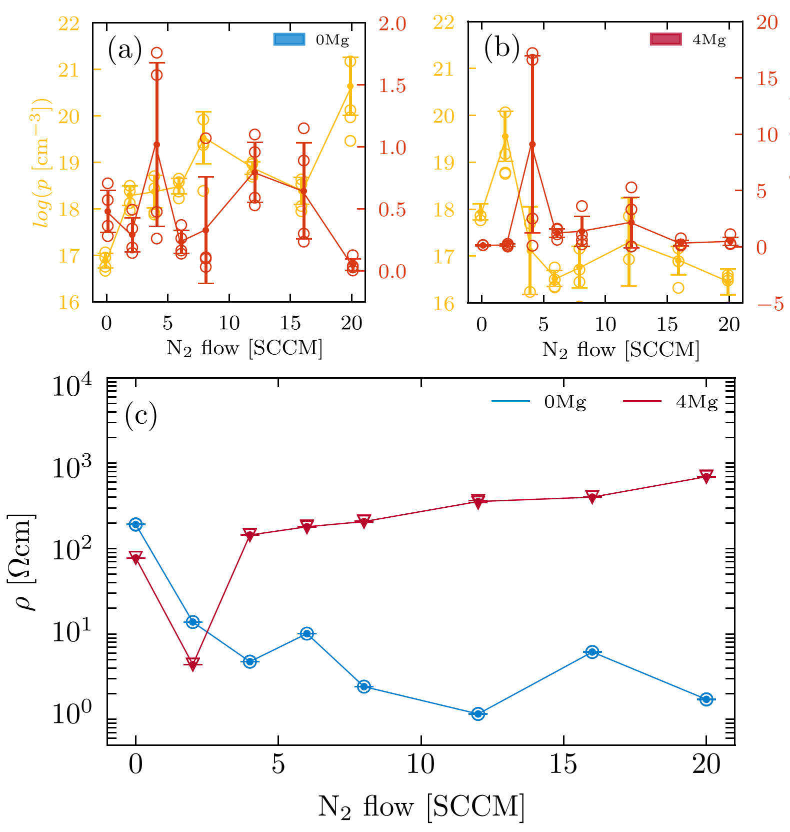


XRD (a) *Phase of copper oxide polycrystalline films deposited from 0Mg target (CuO) shifts from Cu_4O_3 to Cu_2O for increasing N_2 flow, (b) Films from 4Mg target show Cu_2O phase for all N_2 flow values, with increasingly degraded quality.*

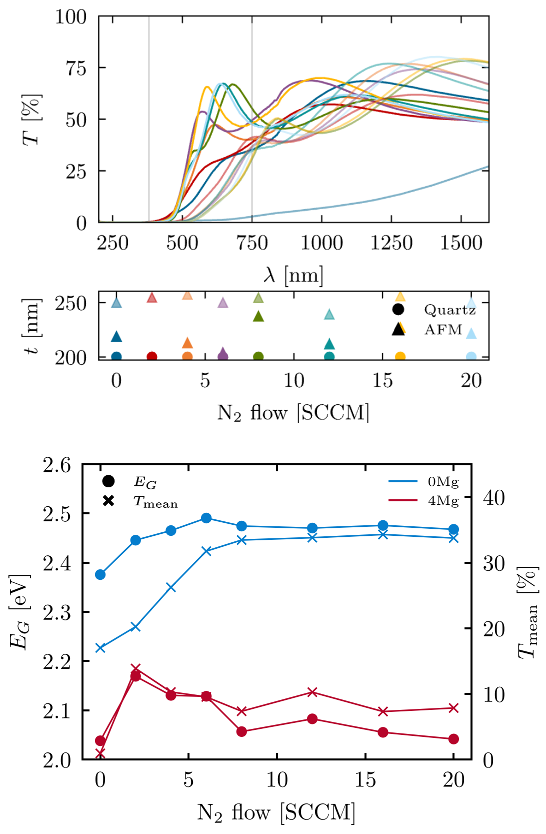
Raman spectroscopy measurements



Electrical characteristics

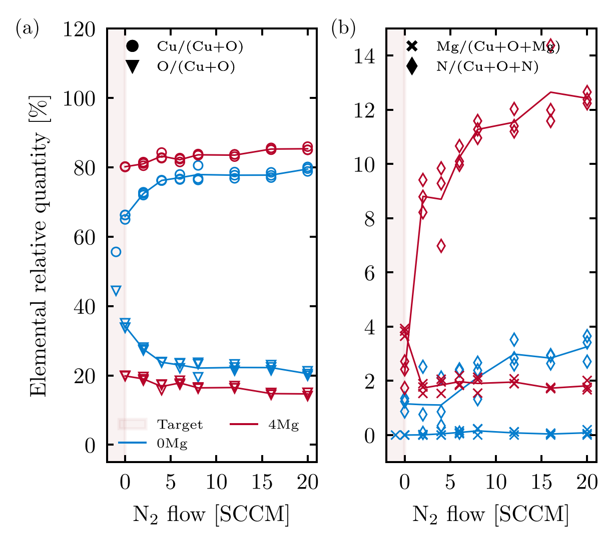


Optical characteristics

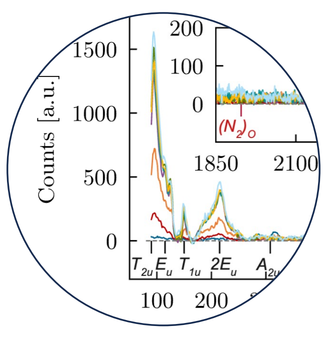


Electrical *Films deposited from 0Mg target show p-type conductivity, with resistivity decreasing by up to 2 orders of magnitude upon N doping due to higher carrier concentrations. (N,Mg) co-doping does not enhance conductivity for large flows.*
Optical *N-doping enhances film transmittance, with lesser optical characteristics for layers with Mg content. Sub-band absorption signal is associated with optical interference. N-incorporation on O site was not observed, i. e. absence of N_O defect.*
Raman *(1) Confirmation of crystalline phase transition from Cu_4O_3 to Cu_2O between 0 and 4 sccm, (2) Identification of $(N_2)_{Cu}$ defect (shallow acceptor) while no band on the $(N_2)_O$ site, (3) All spectra above 4 sccm present similar features between 90 and 800 cm^{-1}*
Compositional *(1) N-incorporation reduces film Mg content, (2) high N-incorporation in the Cu_2O films from the 4Mg target.*

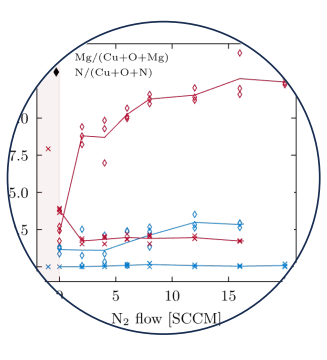
Compositional analysis



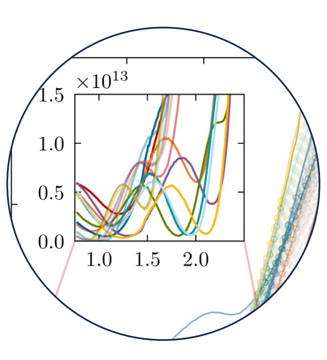
Key learning outcomes



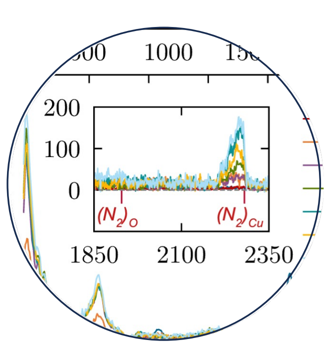
Crystalline transition from CuO (target) to Cu_2O upon in-situ nitrogen doping (> 4 SCCM) (XRD, Raman)



Interaction between N and Mg. Mg presence seems to facilitate a high nitrogen incorporation (EDX, TOF-SIMS)



Subband absorptions identified as interference effect. No N_O point defect detected (Spectrophotometer)



$(N_2)_{Cu}$ shallow acceptor point defect Raman activity proportional to the N_2 deposition flow (Raman)

- Monodoping copper oxide with N or Mg leads to enhanced opto-electrical properties
- (N,Mg) co-doping induces degraded opto-electrical characteristics
- Identification of $(N_2)_{Cu}$ defect as shallow acceptor; no absorption sub-band related to $(N_2)_O$
- High level of N incorporation is associated with lower film quality and amorphisation

References

1. B. Meyer *et al.*, physica status solidi (b) 2012, **249**, 1487–1509.
2. A. Lakshmanan et al., Materials Today Sustainability 2022, **20**, 100244.
3. S. Rühle *et al.*, Sol. Energy 2016, **130**, 139–147.
4. A. Jolk *et al.*, physica status solidi (b) 1998, **206**, 841–850.
5. Y. Wang *et al.*, J. Phys. D: Applied Physics 2021, **54**, 263002.
6. A. Mittiga *et al.*, Appl. Phys. Lett. 2006, **88**, 163502.
7. S. Shibasaki *et al.*, Appl. Phys. Lett. 2021, **119**, 242102.
8. H. Tanaka *et al.*, Thin solid films 2004, **469**, 80–85.
9. T. Minami *et al.*, Appl. Phys. Expr. 2011, **4**, 062301.
10. Y. Nishi *et al.*, J. Vac. Sci. & Tech. A 2012, **30**, 04D103.
11. T. Minami *et al.*, Appl. Phys. Expr. 2013, **6**, 044101.
12. T. Minami *et al.*, Appl. Phys. Lett. 2014, **105**, 212104.
13. T. Minami *et al.*, Energy Mater. Sol. Cells 2016, **147**, 85–93.
14. T. Minami *et al.*, Appl. Phys. Expr. 2016, **9**, 052301.
15. T. K. Wong *et al.*, Materials 2016, 9, 271.
16. L. Y. Isseroff *et al.*, Chem. Mater. 2013, **25**, 253–265.
17. J. Resende *et al.*, physica status solidi (a) 2016, **213**, 2296–2302.
18. M. Nolan *et al.*, Phys. Chem. Chem. Phys. 2006, **8**, 5350–5358.
19. J. Li *et al.*, Sci. Rep. 2014, **4**, 7240.
20. C. Malerba *et al.*, Sol. Energy Mater. Sol. Cells 2012, **105**, 192–195.
21. J. T-Thienprasert *et al.*, Appl. Phys. Lett. 2015, **107**, 221905.

Acknowledgements

TCM-TOEO 2025
Rethymno, October 19th - 23rd

Check our other contributions at TCM-TOEO 2025 !

O12 (20/10) - F. Balty *et al.*, *Insight into the morphological instability of metallic nanowires under thermal stress*
O25 (21/10) - A. Baret *et al.*, *Heuristic approach to the fundamental optical constants of silver nanowire networks: experiments and theory*
Posters : F. Balty *et al.* *Electrical failure in microscale silver nanowire networks under voltage pulses*
A. Baret el al. *Thermal emissivity of silver nanowire networks : a characterization tool for instability studies*