Crystalline phase transitions and point defects in nitrogen and magnesium-doped copper oxide thin films deposited by magnetron sputtering under optimized pressure conditions

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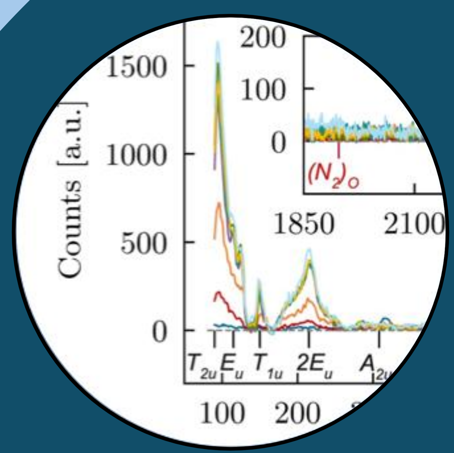
Abstract

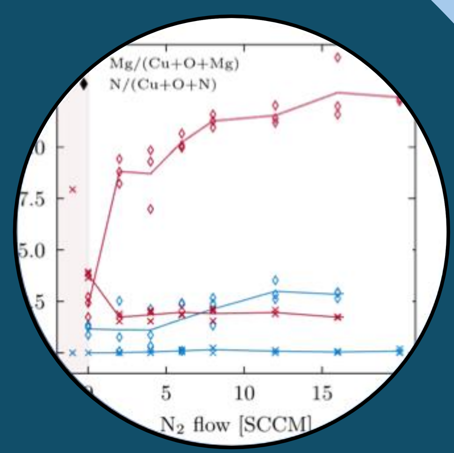
Cu_2O is a promising transparent conducting oxide for photovoltaic applications, with a large absorption coefficient and *p*-type conductivity. Additionally, this material is abundant and nontoxic and can be synthesized using various chemical and physical routes [1]. The objective of this work is to extend the understanding of the role of point defects in intentionally doped copper oxide thin films. Moreover, this work contributes to the assessment of Mg and N as doping species through extensive material characterization including X-ray and Raman spectroscopy measurements.

Introduction

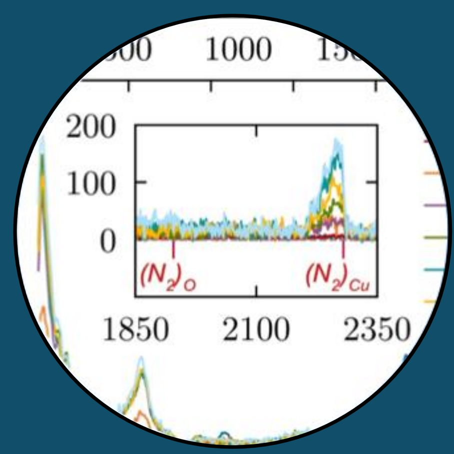
Key takeaways



Crystalline transition from CuO to Cu_2O upon *in-situ* N doping (XRD, Raman)



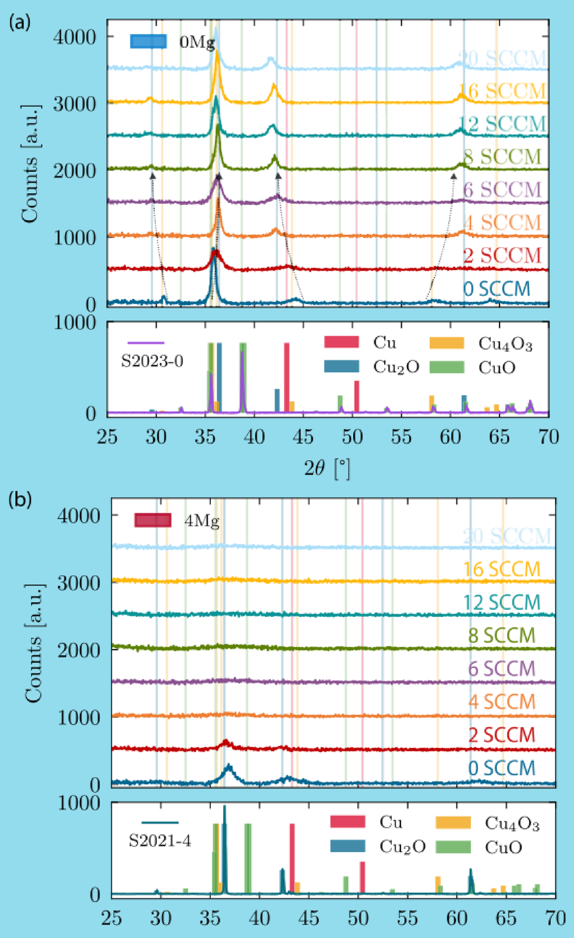
Mg presence seems to facilitate a high N incorporation (EDX, TOF-SIMS)



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

XRD and Raman analyses

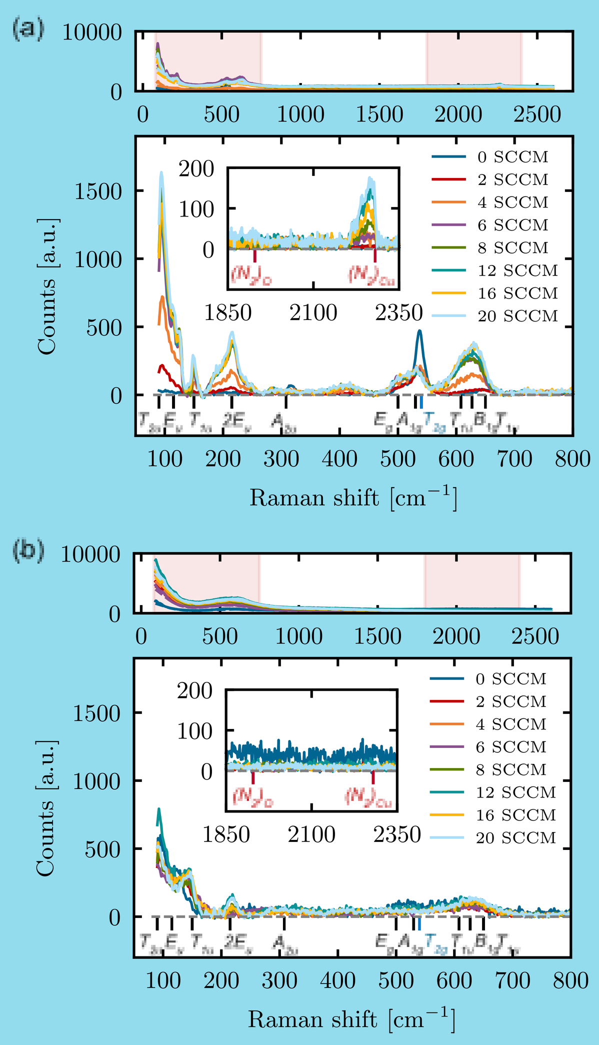
XRD spectra



(a) Thin films deposited from 0Mg target (CuO) **shifts** from Cu_4O_3 to Cu_2O **for increasing** N_2

(b) Thin films from 4Mg target show **Cu_2O phase** for all N_2 flow values, with **increasingly degraded** quality.

Raman spectroscopy



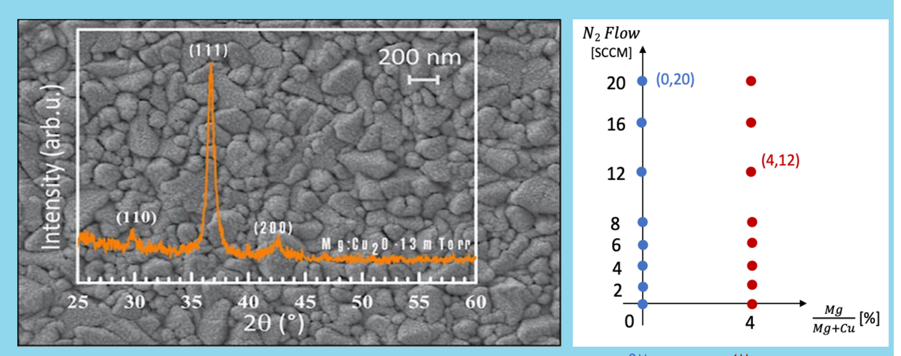
- Confirmation of **crystalline phase transition** from Cu_4O_3 to Cu_2O between 0 and 4 sccm
- Identification of $(N_2)_{Cu}$ defect (shallow acceptor), no band on the $(N_2)_O$ site
- All spectra above 4 sccm present similar features between 90 and 800 cm^{-1}

Methods

RF-sputtering

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

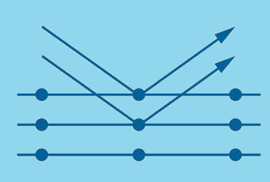
Cu_2O thin film



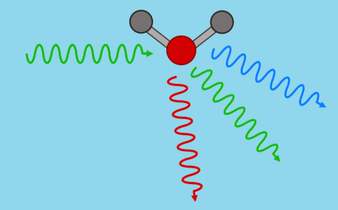
N. Sliti et al., Ceram. Int., 48(16), 23748-23754 (2022)

Measurements

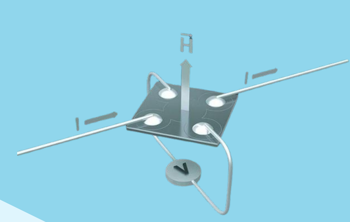
XRD



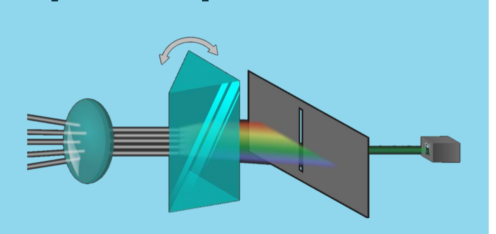
Raman



Van der Pauw



Spectrophotometer



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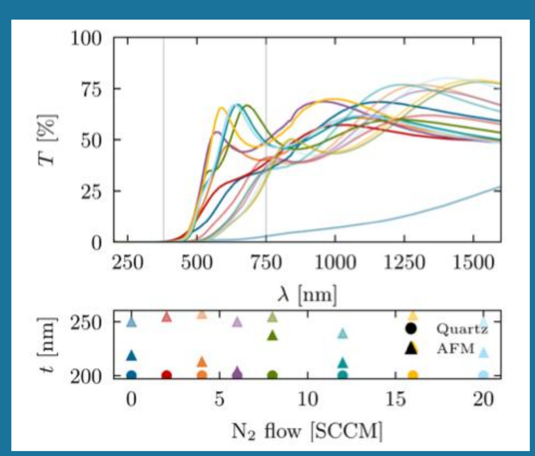
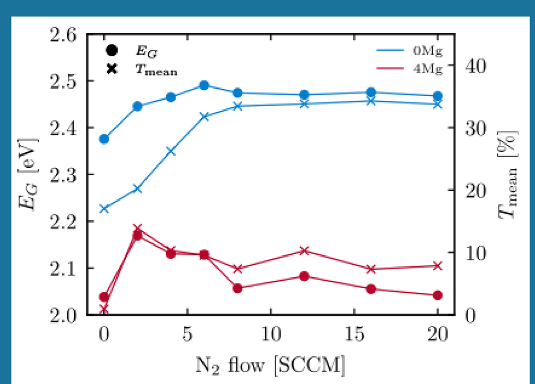
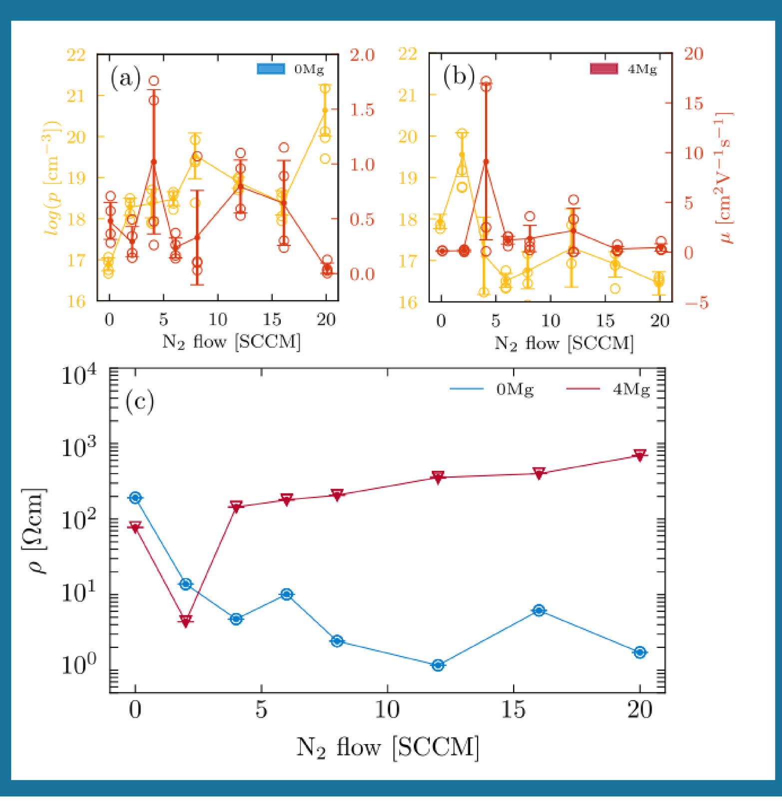
Properties

Optical





Electrical

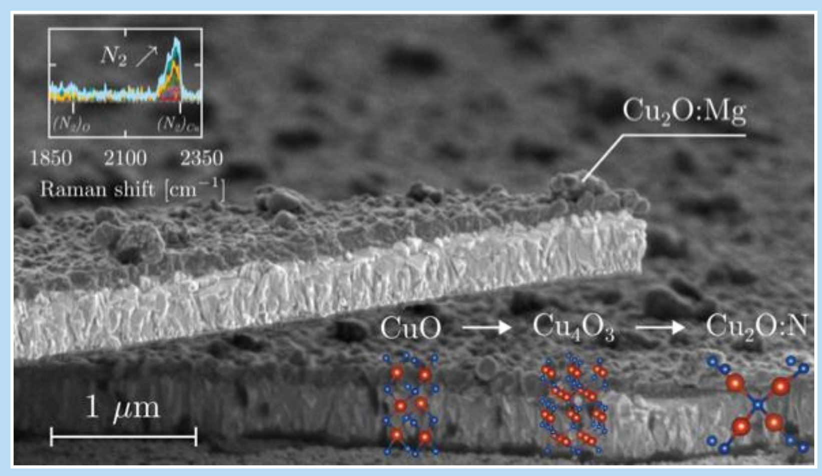


- *P*-type conductivity, with **resistivity decreasing** by up to 2 orders of magnitude upon **N doping** due to **higher carrier concentrations.**
- *N*-doping **enhances** film **transmittance**. *N*-incorporation on O site was not observed, *i.e.* **absence** of N_O defect.

Conclusions

In summary

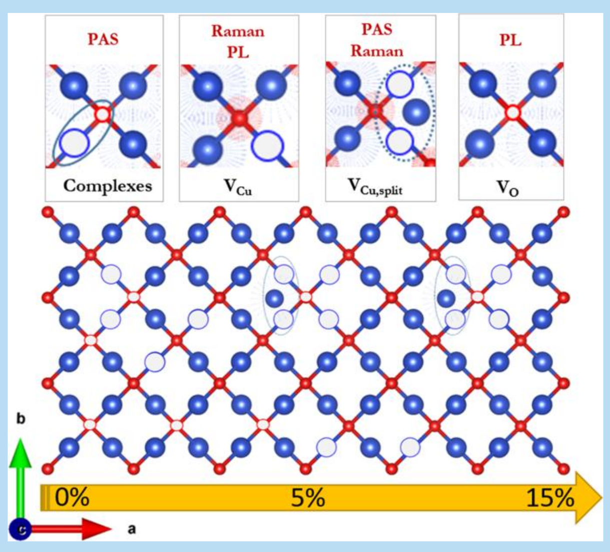
- **Key** role of **XRD** in this study



T. Ratz et al., ACS Appl. Electron. Mater. 7 (2), 643–651 (2025)

- **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
- **High** level of **N incorporation** is associated with **lower** film **quality** and **amorphization**

Perspectives



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- Control of the **O flow** during the thin film synthesis to better control **defects**
- **Photoluminescence** and advanced measurements such as Positron Annihilation Spectroscopy (PAS)

References

[1] B. Meyer *et al.*, physica status solidi (b), 249, 1487–1509 (2012).
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Acknowledgments

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