A study of the defect formation of CuO nanostructures under He^{+} ion irradiation

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2. Experimental technique
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   b) CuO irradiated. XRD, DBS and PALS.
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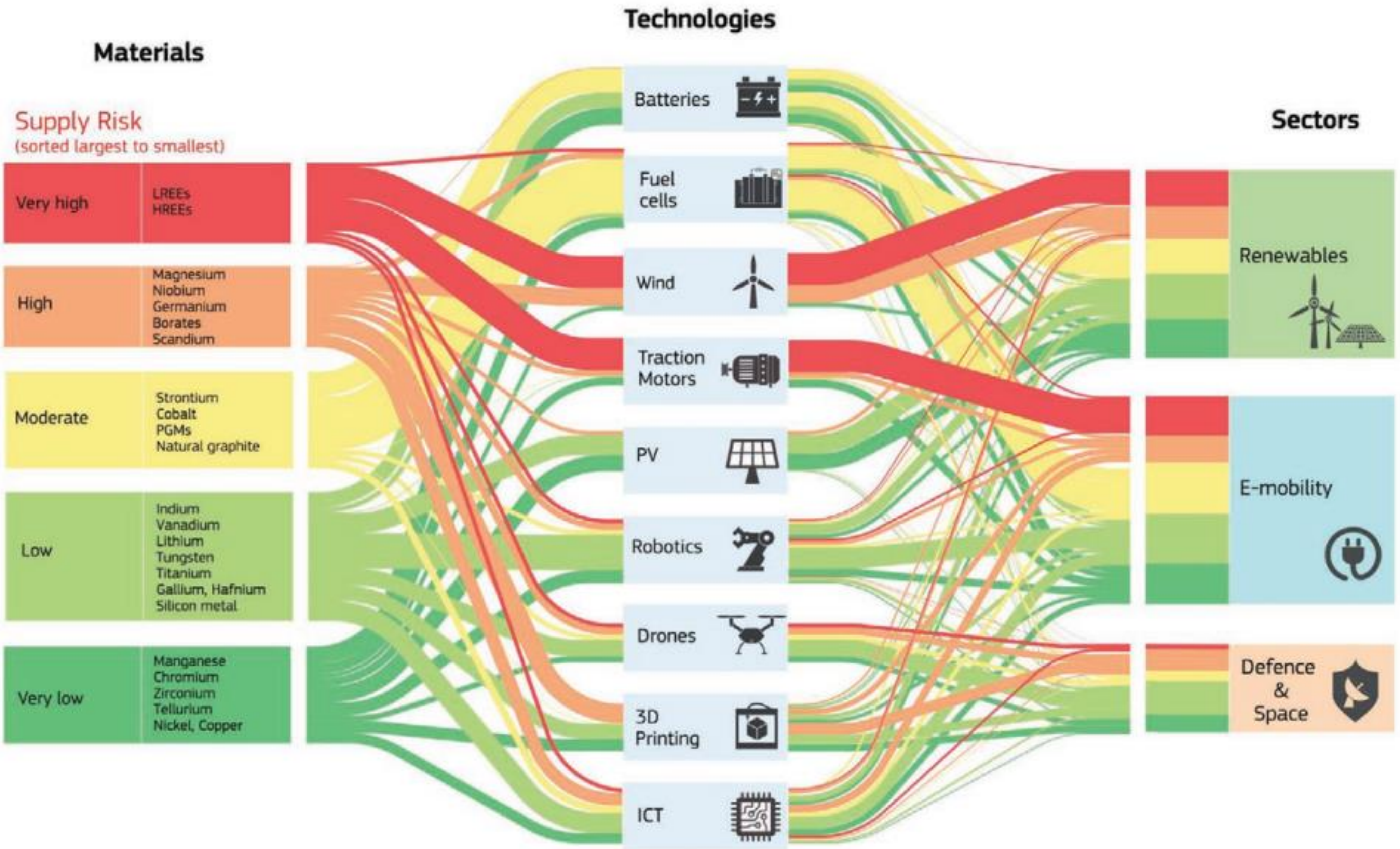
1. Introduction. CuO properties.



1. Introduction. CuO properties.

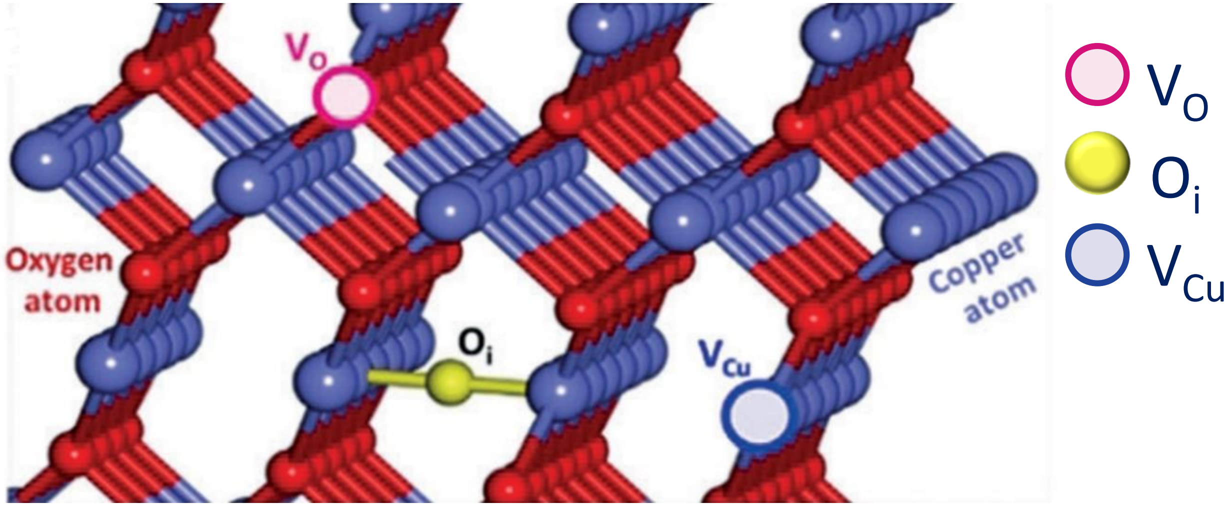
Properties:

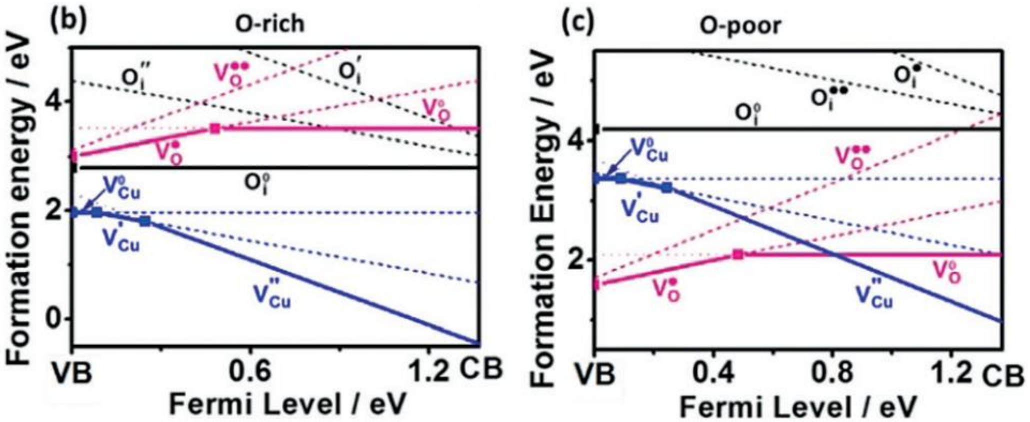
- Non-toxic and abundant in the Earth's crust.
- Easy to obtain by low-cost techniques.
- p-type semiconductor with a narrow bandgap of 1.2-2.16 eV.
- Low hole mobility 0.1-10 $\frac{cm^2}{V \cdot s}$
- Electronic conductivity $1.05 \cdot 10^{-2}$ and $6.30 \cdot 10^{-2} (\Omega \cdot cm)^{-1}$.
- The dominant defects in CuO are the copper vacancies (V_{Cu}).

How to modify CuO properties?

- thermal treatments,
- doping,
- nanocompounds,
- irradiation.

Types of defects in CuO





Defect reactions:

$$O_O \rightarrow V_O^{x\bullet} + xe' + 1/2O_2$$

$$1/2O_2 \rightarrow V_{Cu}^{x'} + xh^\bullet + O_O$$

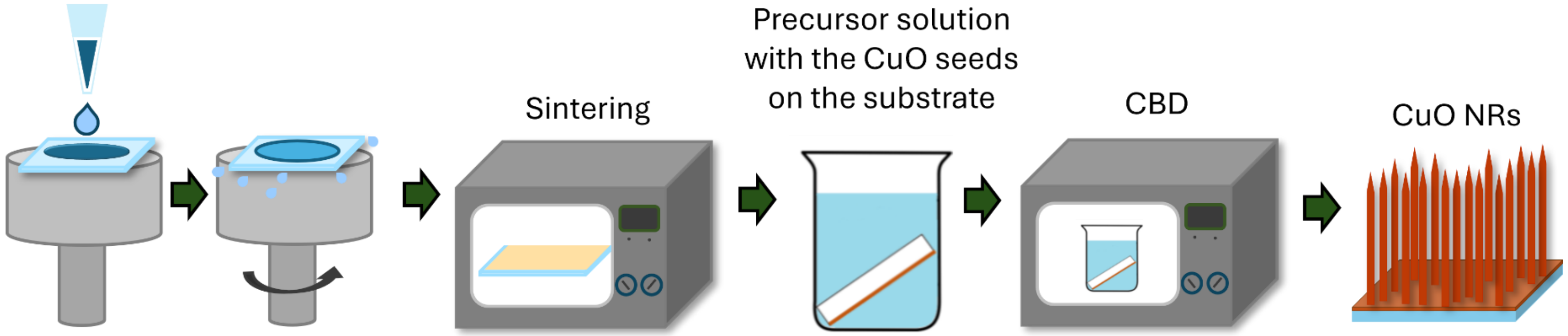
$$1/2O_2 \rightarrow O_i^{x'} + xh^\bullet$$

[Wang, 2019]

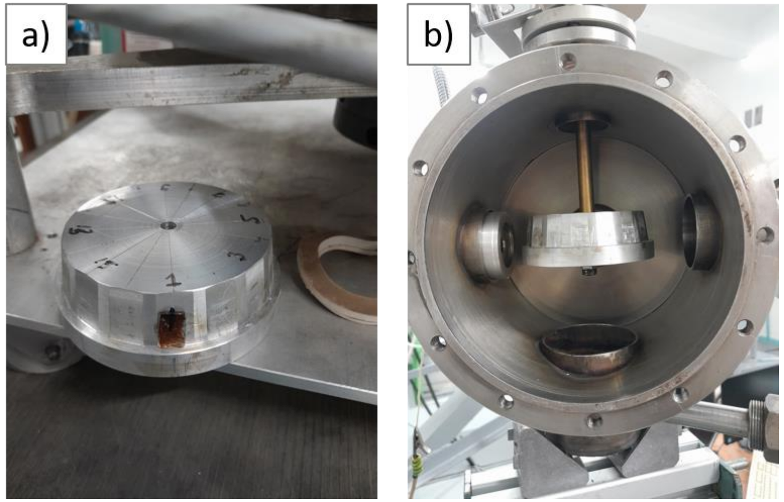
2. CuO nanostructures synthesis and irradiation

CuO seeding process

CuO elongated nanostructures synthesis



Sample holder and irradiation

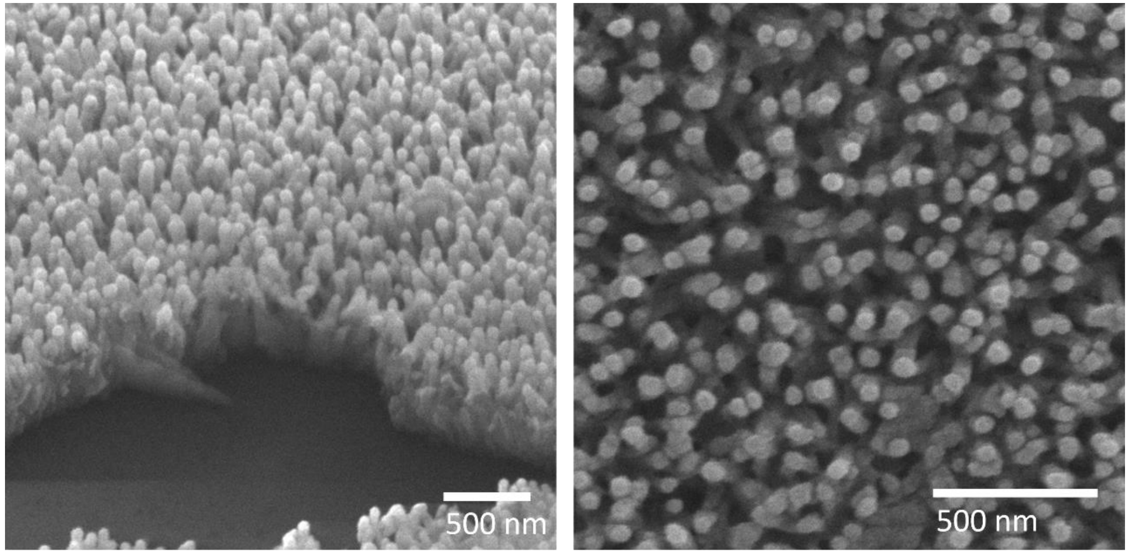


CuO irradiated samples parameters

Sample	Dosis (part/cm^2)	time (s)
CuO reference	0	0
CuO_10	$3.13\cdot10^{13}$	10
CuO_100	$3.13\cdot10^{14}$	100
CuO_1000	$3.13\cdot10^{15}$	1000
CuO_5000	$3.13\cdot10^{16}$	5000
CuO_3h	$3.38\cdot10^{16}$	10 800

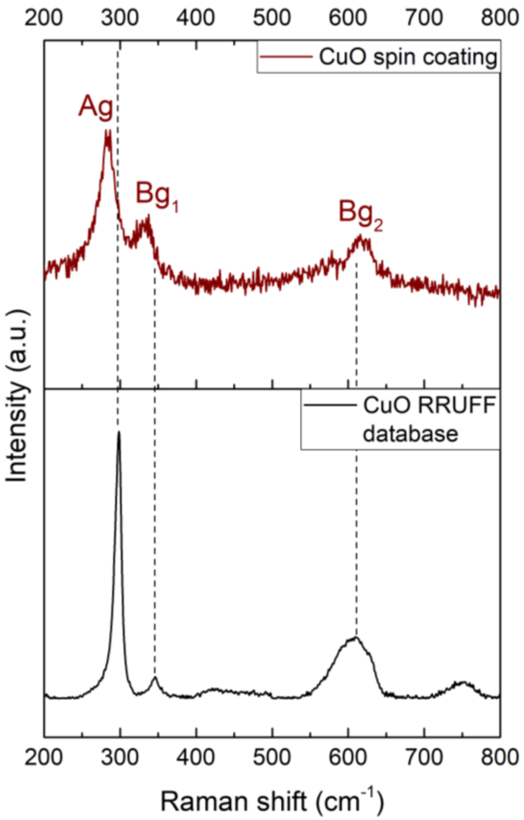
3.1. CuO nanostructures

SEM

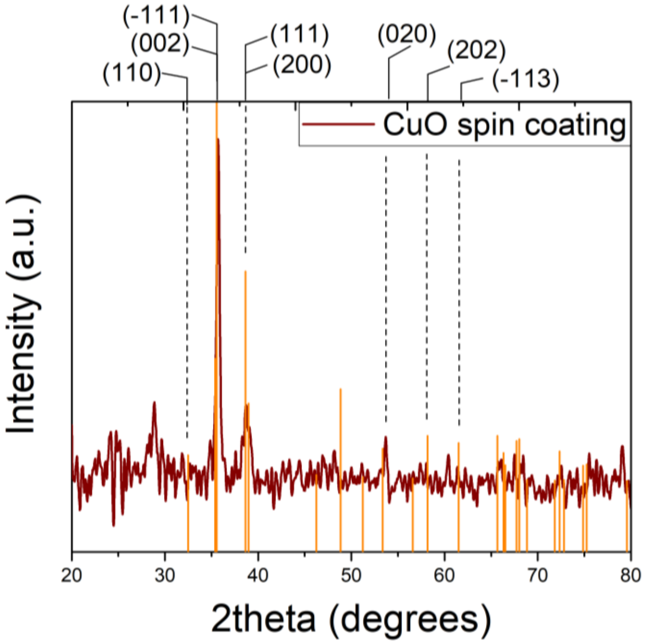


- CuO structures with elongated morphology.
- CuO nanostructures diameter was calculated to be (64 ± 1) nm.
- CuO nanostructures height was estimated to be about 430 nm.

Raman spectroscopy



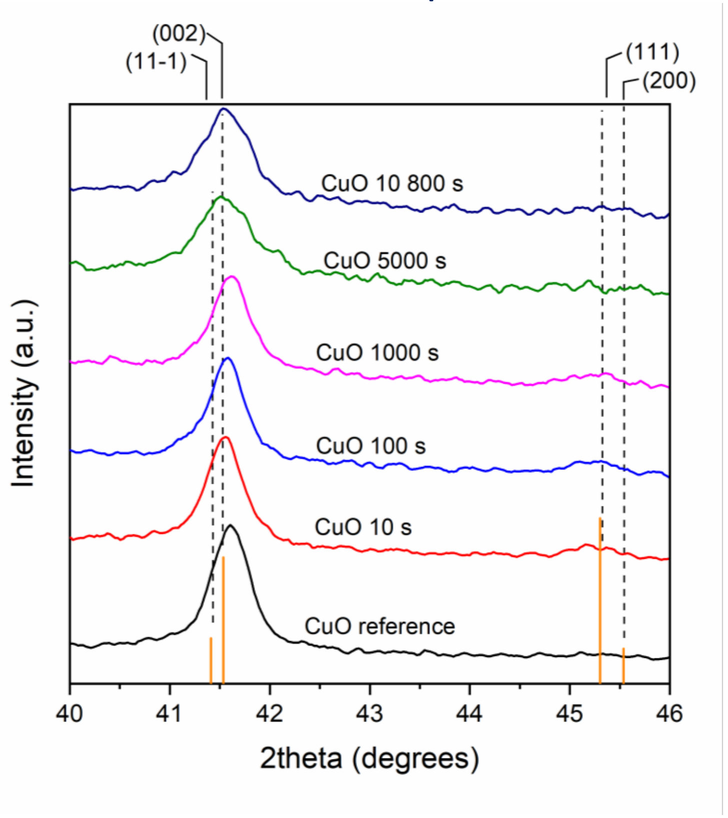
XRD



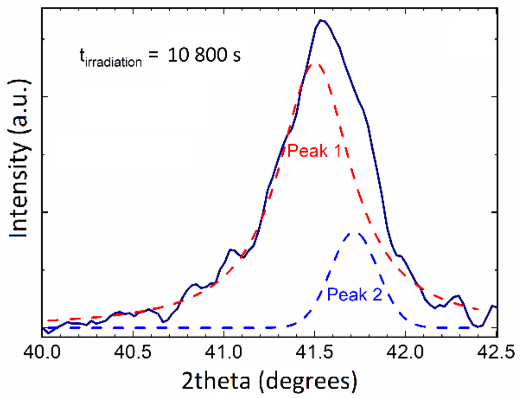
- Raman spectroscopy and XRD confirm the presence of CuO with a monoclinic structure in the samples.
- The XRD pattern shows a preferential orientation in the direction [001].

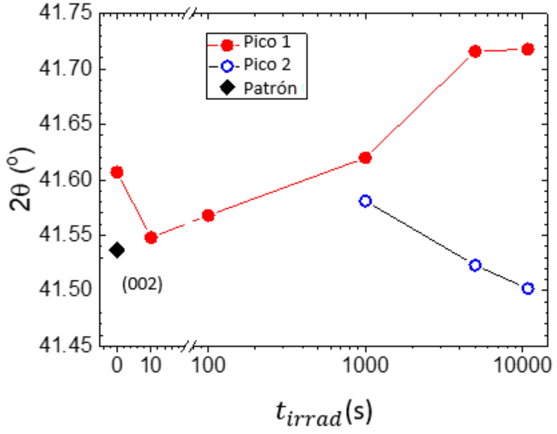
3.2.1. CuO irradiated nanostructures: XRD

XRD difractograms of the irradiated samples

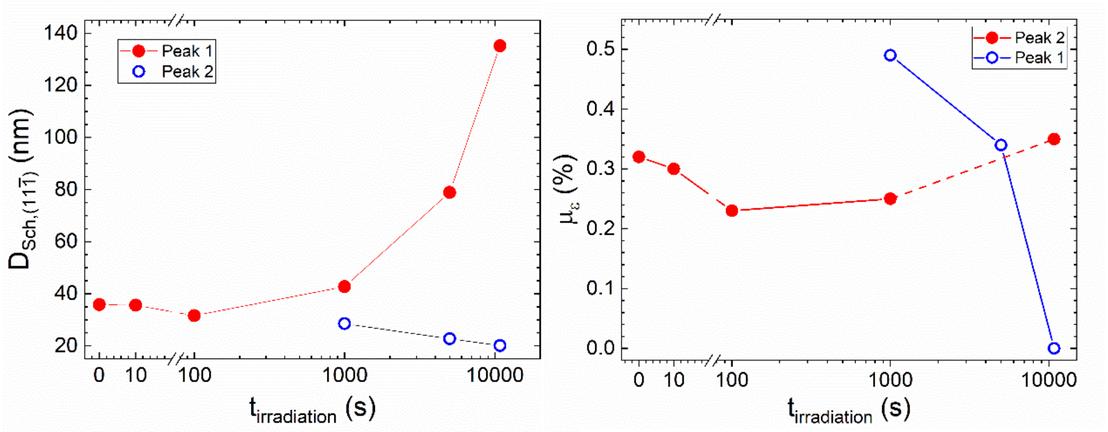


Deconvoluted diffraction maxima (11-1)(002)





Crystallite size and strain



- Increase in dosis produce bigger crystallites and more strain.

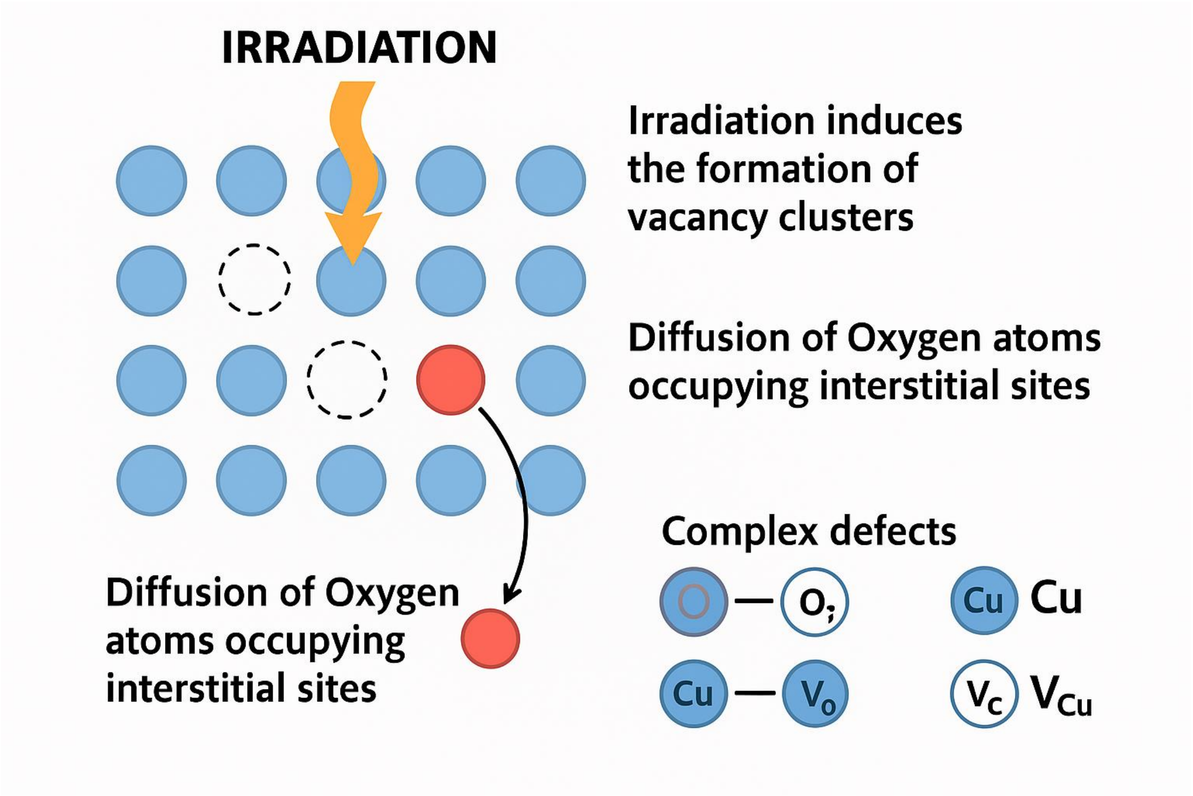
- 2theta decreses at t_{irrad} <10 s dosis.
- 2theta increases at higher dosis.
- Cristalline lattice under tensión.

- 2nd peak shift to low 2theta at higher dosis: cristal lattice locally tenses.

3.2.1. CuO Irradiated nanostructures: XRD

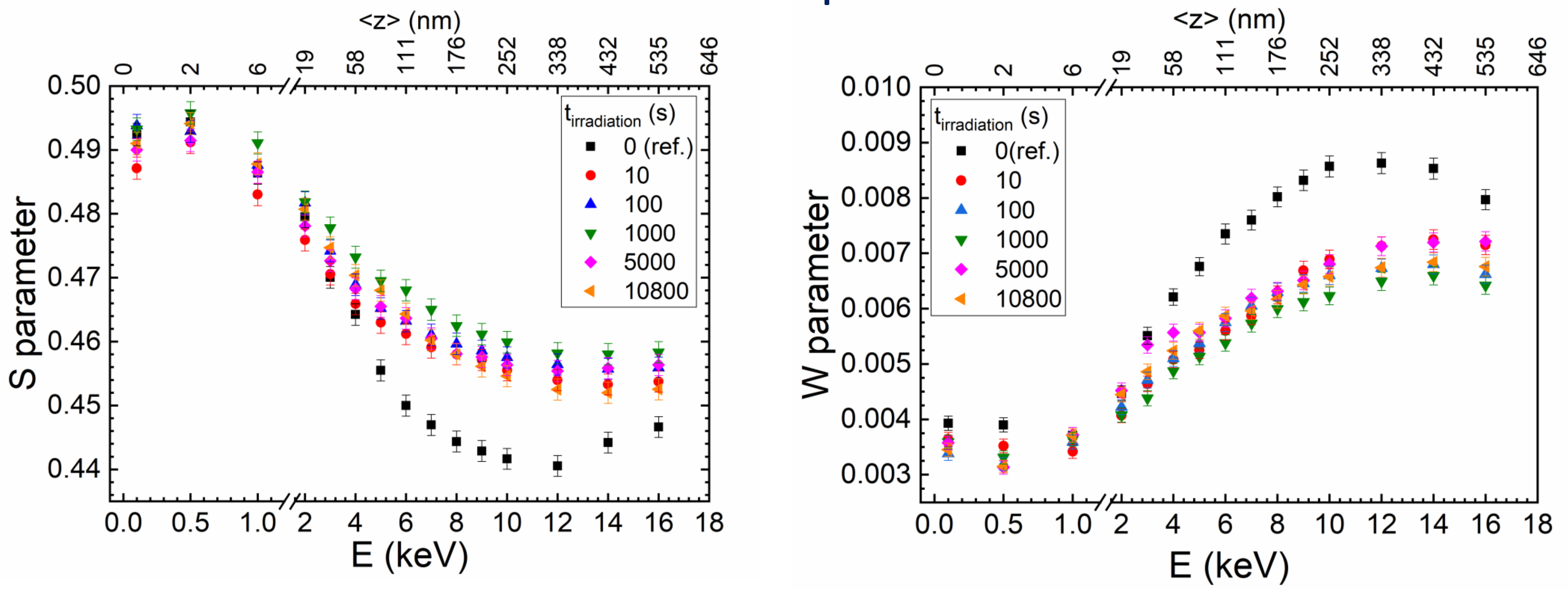
Influence of the irradiation in the lattice:

1. formation of vacancy clusters.
2. diffusion of Oxygen atoms from their original positions in the lattice, occupying interstitial sites (O_i).
3. complex defects such as Cu-V_O or Cu$-V_{Cu}$.



3.2.2. CuO Irradiated nanostructures: DBS

S and W parameters

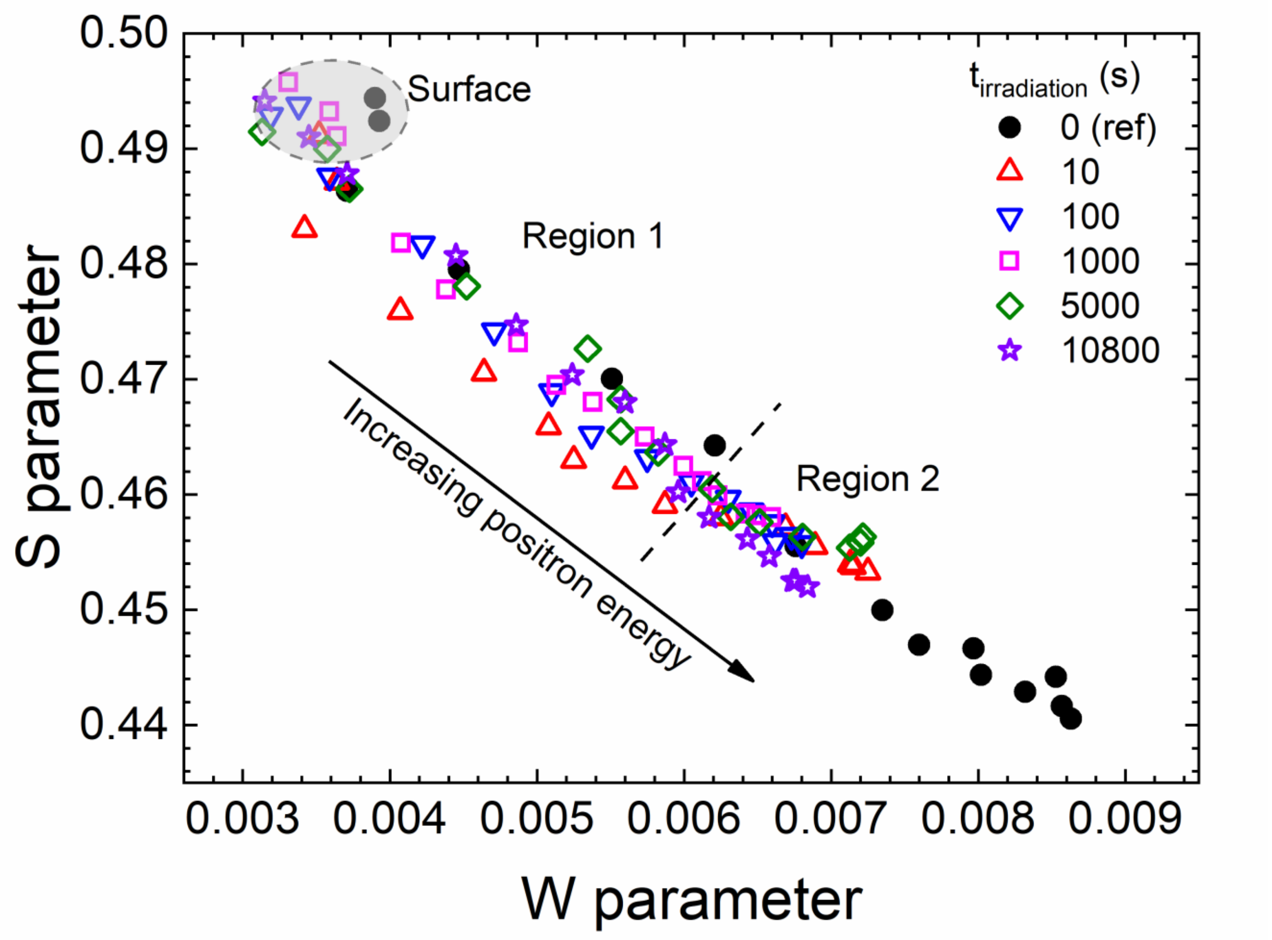


- The increase in **S** parameter indicates that the number of monovacancies (V_{Cu}, V_O), in the material increases.
- Low doses: defects are generated by irradiation.
- High doses: punctual defects form clusters.

Competition between:
Irradiation and the CuO lattice recovery.

3.2.2. CuO Irradiated nanostructures: DBS

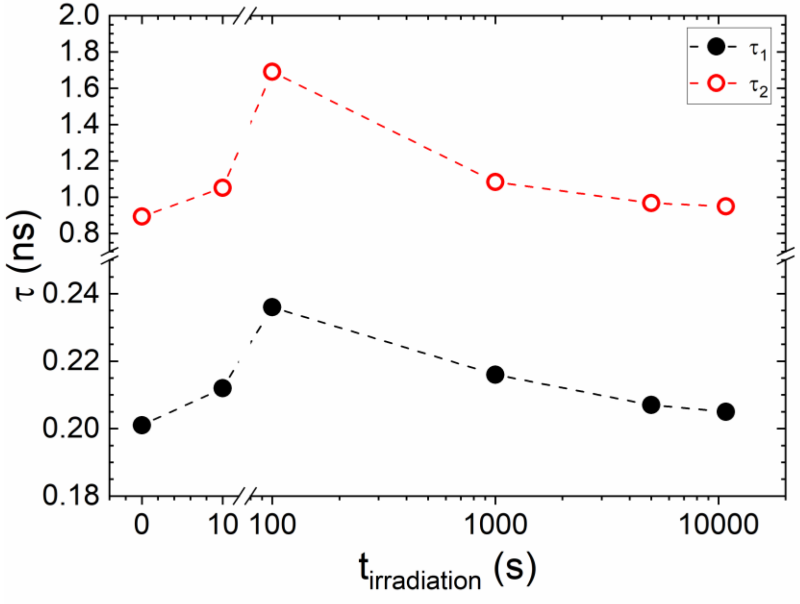
Correlation between S and W



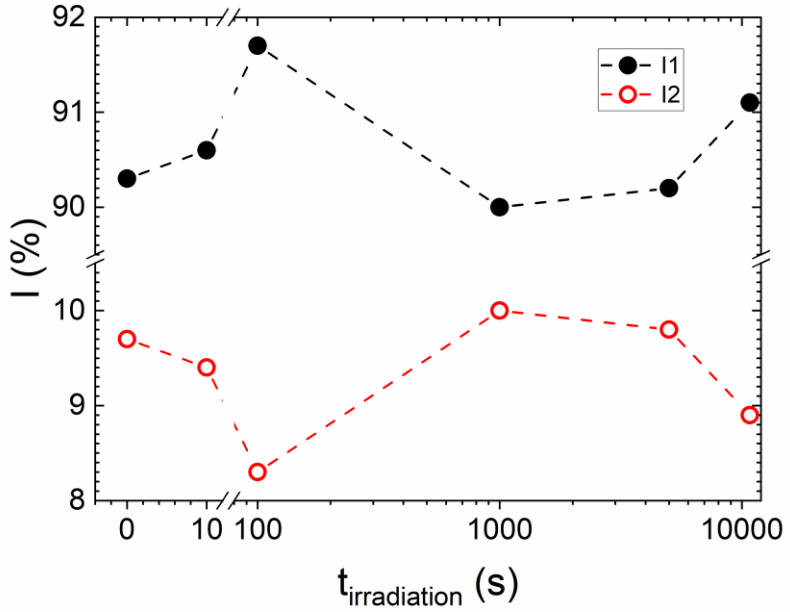
The inequality between regions 1 and 2 is due to the considerable difference between their slopes (trapping fractions).

3.2.3. CuO Irradiated nanostructures: PALS

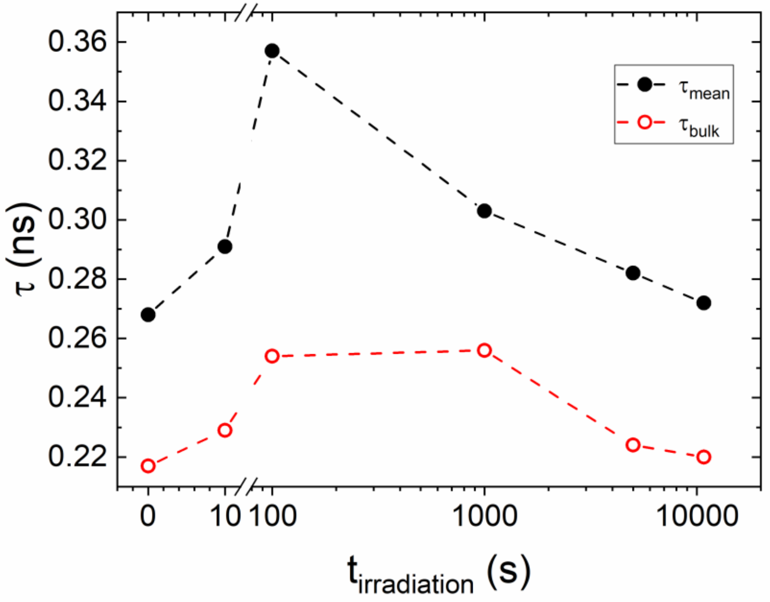
CuO positron lifetimes



Intensities



Average and bulk lifetimes



- These lifetimes correspond to V_{Cu}.
- At higher t_{irrad} τ decreases until 0.205 ns.
- $\tau_2 \geq 0.893$ ns are correlated with vacancy clusters present on the surfaces of the nanostructures.

- I_1 → 90-91.7 %: $\boldsymbol{V_{Cu}}$ **predominant defect.**
- I_1 shows similar behavior to τ_1, except in CuO 3h. This indicates that the defect concentration does not increase.
- defects associated to I_2 large in size but low in concentration.

- τ_{ave} and τ_{bulk} exhibit a similar behavior to τ_1 y τ_2.
- τ_{ave} and τ_{bulk} decreases about a 35% at **higher dosis due to a decrease of superficial and bulk vacancies.**

3.2.3. CuO Irradiated nanostructures: PAS

Influence of the irradiation in the lattice:

1. Increase of monovacancies ($\boldsymbol{V_{Cu}}$, V_O), with the dosis.
2. Formation of punctual defect clusters.
3. $\boldsymbol{V_{Cu}}$ predominant defect.
4. Higher dosis: decrease of superficial and bulk vacancies.

CuO nanostructures conductivity increase!!

4. Conclusions

This work exposed the results of the structural and morphological analysis and the evolution of defects in irradiated copper (II) oxide nanostructures. For this purpose, CuO was subjected to helium ion irradiation treatment. This process led to novel results regarding the influence of irradiation on CuO nanostructures. Specifically, concerning to structural variations, since the irradiated samples show novel results because the defects induced by irradiation compete with the recovery of the crystal lattice. Besides, this irradiation produce a large amount of $\boldsymbol{V_{Cu}}$ the type of defect that is predominant and produce holes, increasing the CuO conductivity. This improvement contributes to produce better CuO nanostructured layers for optoelectronics applications.

A study of the defect formation of CuO nanostructures under He+ ion irradiation

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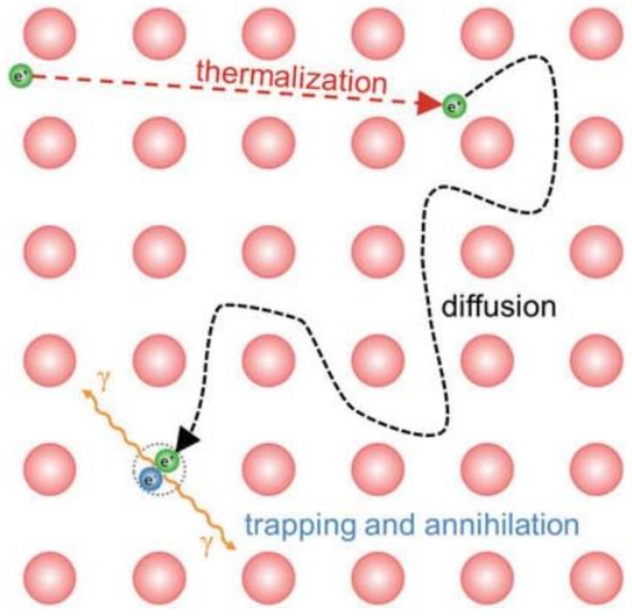
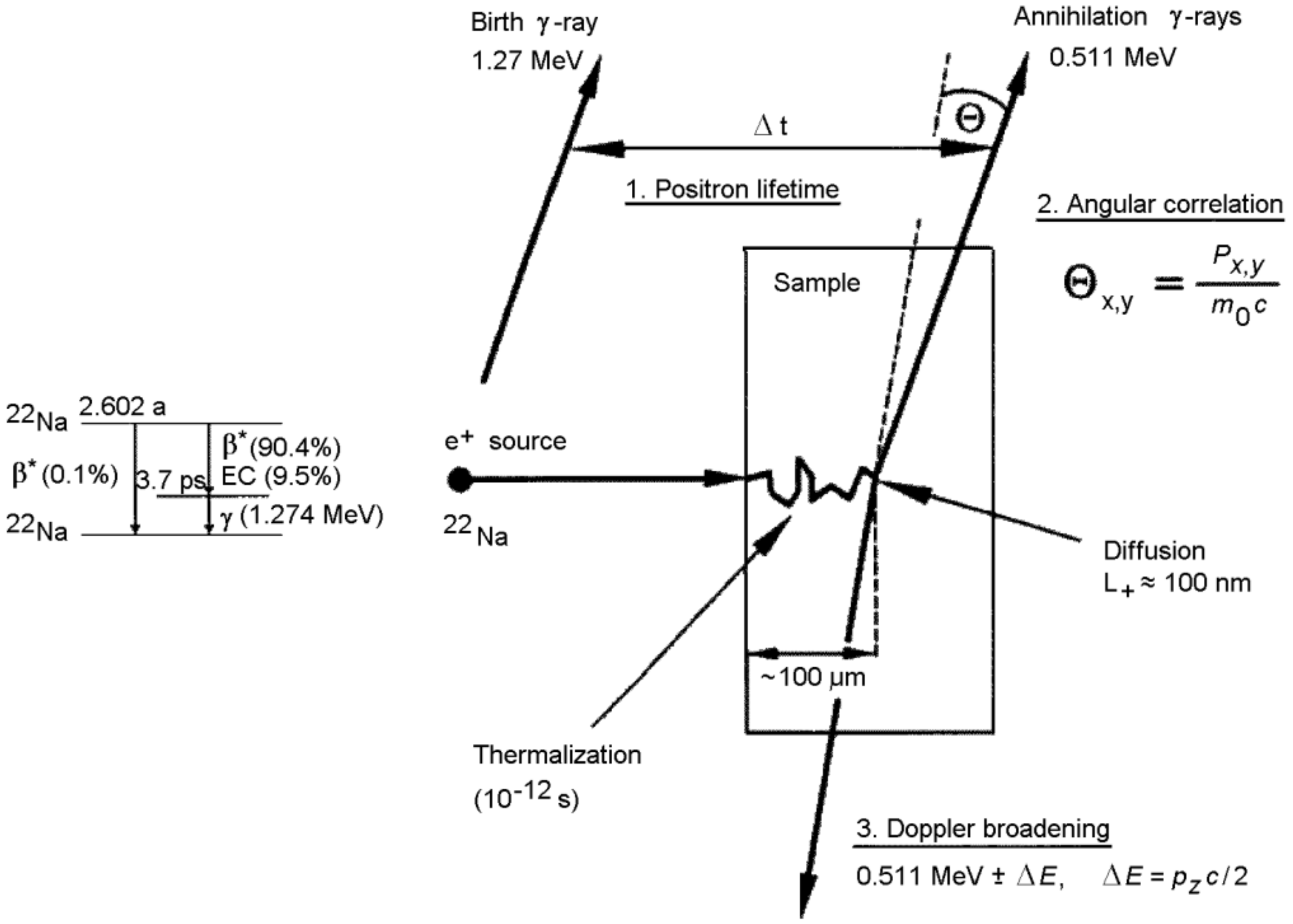
Principio de detección de defectos en PAS

Esquema de los procesos posteriores a la implantación del e+



Bases de PAS

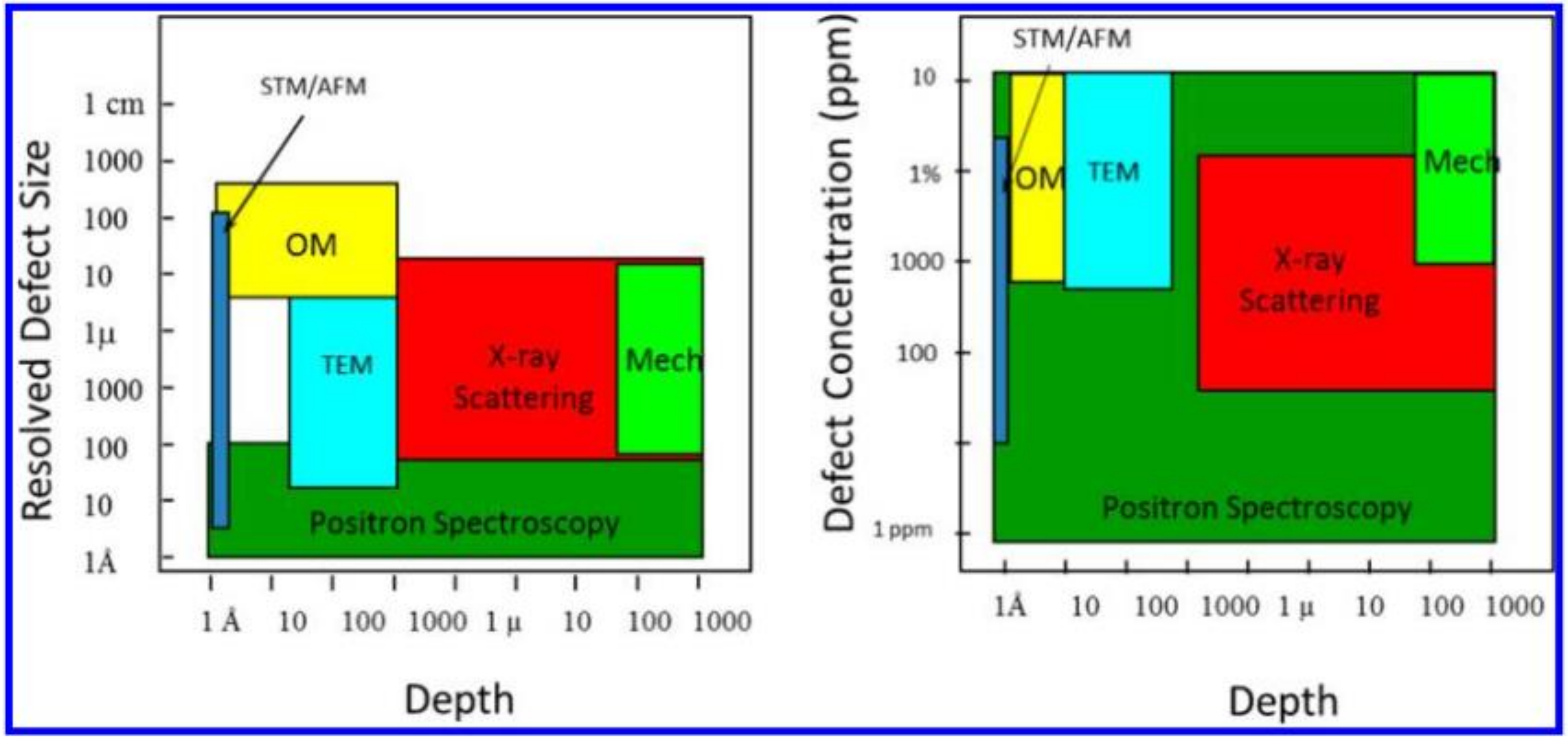


[Chiari y Fujinami, 2019 and Zhu 2007]

PAS advantages

- It is the only technique that can identify vacancies of atomic dimensions and provides information about:
  - size,
  - structure and
  - concentration (10^{-7}).

- not destructive,
- not sensitive to lattice parameter variations,
- does not measure the effect that defects produce on the properties of materials and
- higher resolution than TEM.

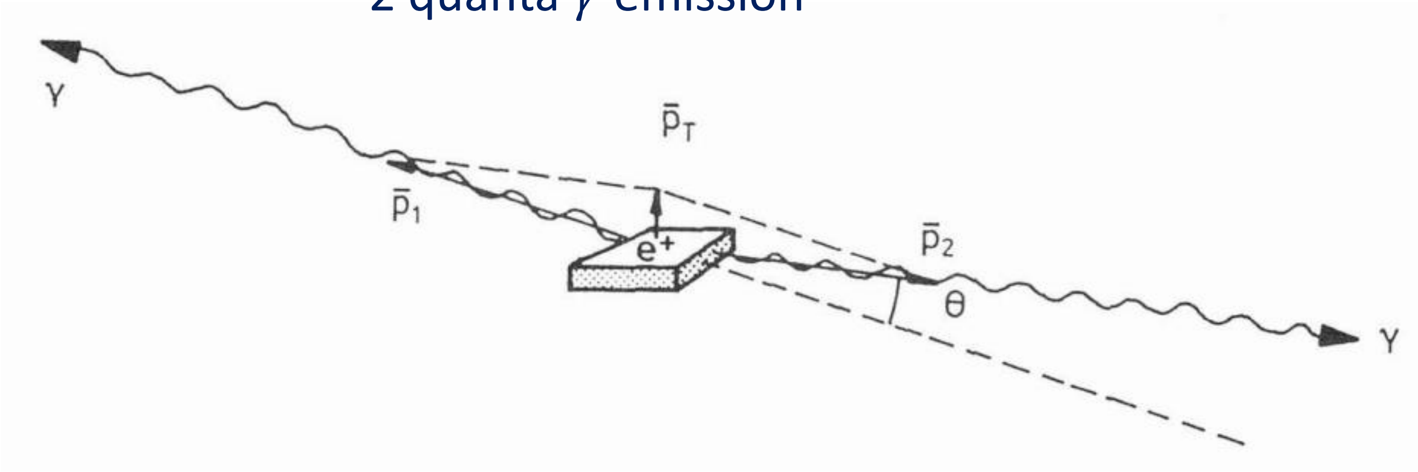


TEM: transmission electron microscopy, **STM**: scanning tunneling microscopy, **AFM**: atomic force microscopy, **OM**: optical microscopy, **Mech**: mechanical method

[Jean, 2013]

5. Introduction to PAS. Positron. History

2 quanta γ emission



1928: Dirac predicts the positron.

1932: Anderson discovers the positron in a cloud chamber.

1940: PAS is used to study:

- Fermi surface in metals and semiconductors.
- Electron density functions.

1960: positron trapping is discovered.

Applications:

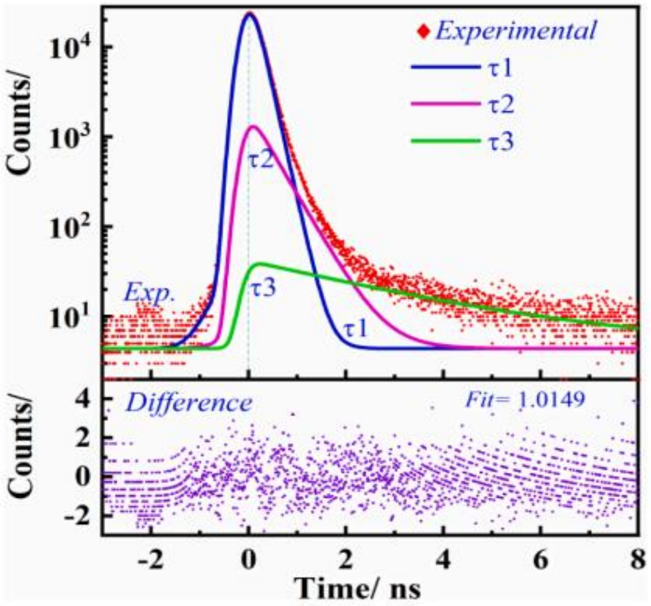
- Astrophysics
- Particle physics
- Biomedicine
- Materials Science

[Eldrup, 1995]

Types of PAS

Positron Annihilation Lifetime Spectroscopy (PALS)

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \, exp\left(\frac{-t}{\tau_i}\right)$$



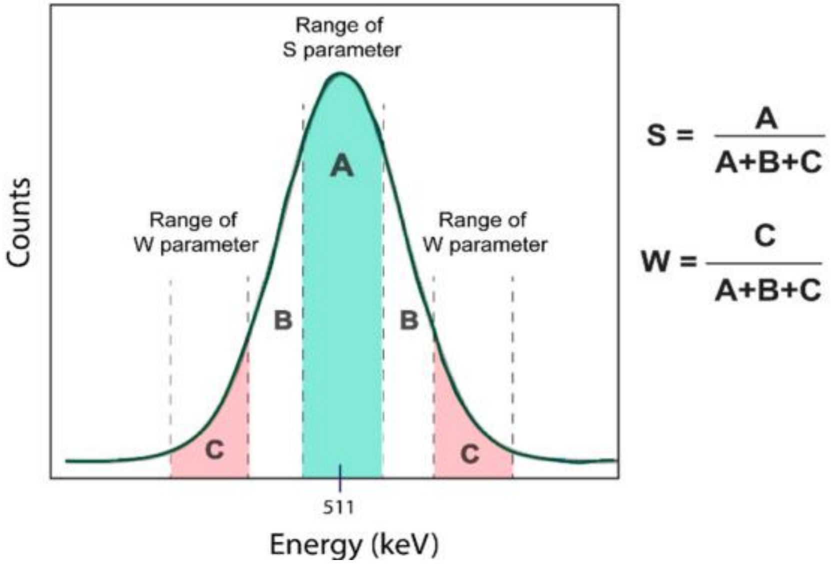
[Selim, 2021]

Softwares: PAFIT [Olsen] y LT [Kansy]

Doppler Broadening Spectroscopy (DBS)

ΔE (Doppler shift)

$$\Delta E = \frac{cp_z}{2}, \text{ 511 eV}$$



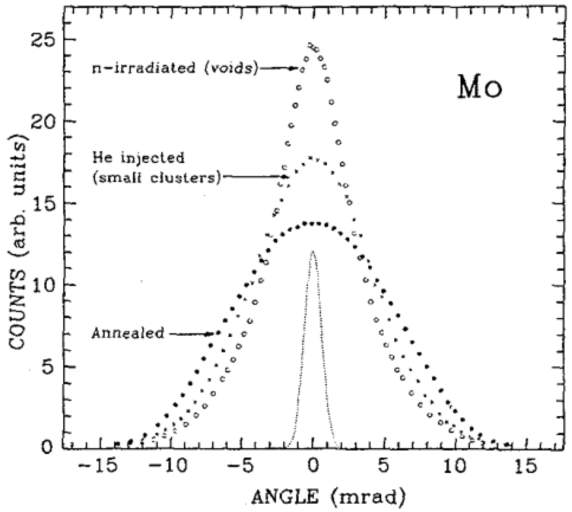
[Selim, 2021]

Software: SP [Dryzek]

Angular Correlation of Annihilation Spectroscopy (ACAR)

ΔΘ

$$\Delta\Theta_{x,y} = \frac{p_{x,y}}{mc}, \text{ 511 eV}$$



[Eldrup, 1995]

Tipos de Espectroscopía de aniquilación positrónica (PAS)

Tipos de PAS

Positron Annihilation Lifetime Spectroscopy (PALS)

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} exp\left(\frac{-t}{\tau_i}\right)$$

- Each type of defect has a characteristic positron lifetime.
- Information about the size and structure of the defect.

Doppler broadening spectroscopy (DBS)

ΔE (Doppler shift)

$$\Delta E = \frac{cp_z}{2}, 511 \text{ keV}$$

- Doesn´t provide information about the size of the defects.
- Qualitative information on changes about defect types based on the S-W correlation.

Angular correlation of annihilation radiation (ACAR)

ΔΘ

$$\Delta\Theta_{x,y} = \frac{p_{x,y}}{mc}, 511 \text{ keV}$$

- Information about the electronic structure.
- More detailed information than PALS.
- More complex processing.

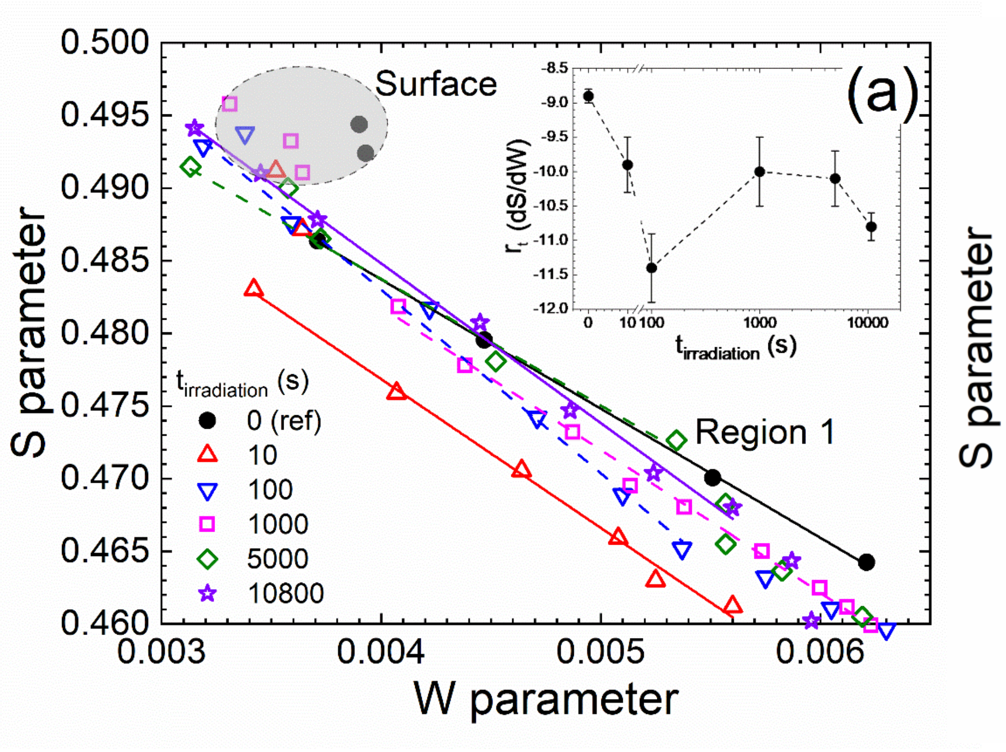
[Eldrup, 1995 y Selim, 2021]

Materials and methods. Equipment

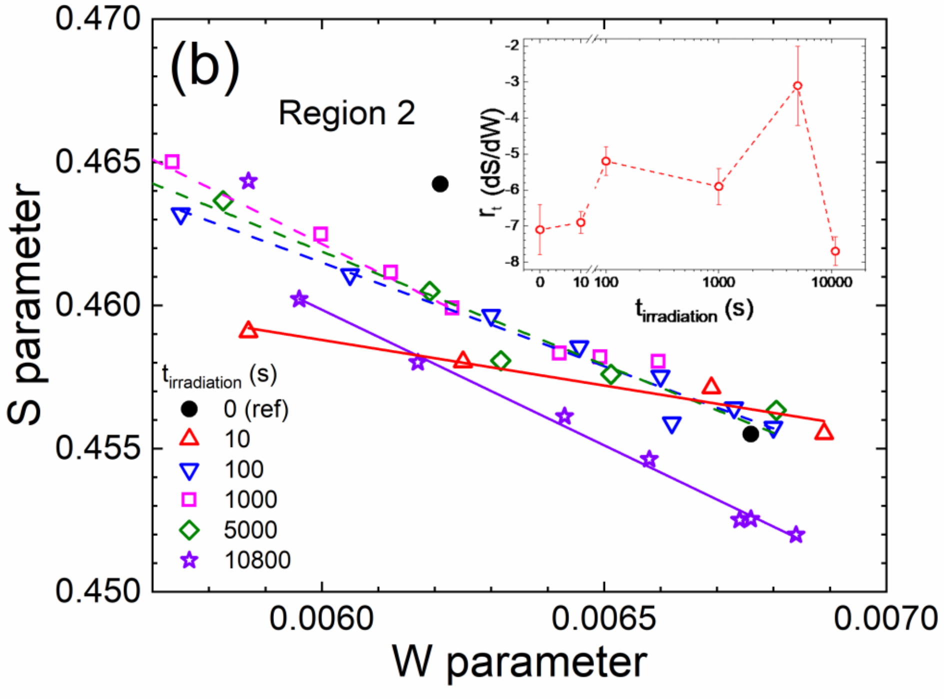
Characterization technique	**Equipment**	**Institution**	**Country**
SEM	Tescan Vega	IMRE	Cuba
Raman	Horiba Jobin-Yvon LabRAM, Horiba (iHR320)	IJL,INRS	France, Canada
XRD	Diffractometer PANanalytical EMPYREAN Co K_α1=1.78892 nm	JINR	Russia
FTIR	Bruker Tensor 27	IMRE	Cuba
RBS, Irradiación	Van der Graaff accelerator	JINR	Russia
Positron annihilation (PAS)		JINR	Russia

CuO Irradiated nanostructures: DBS

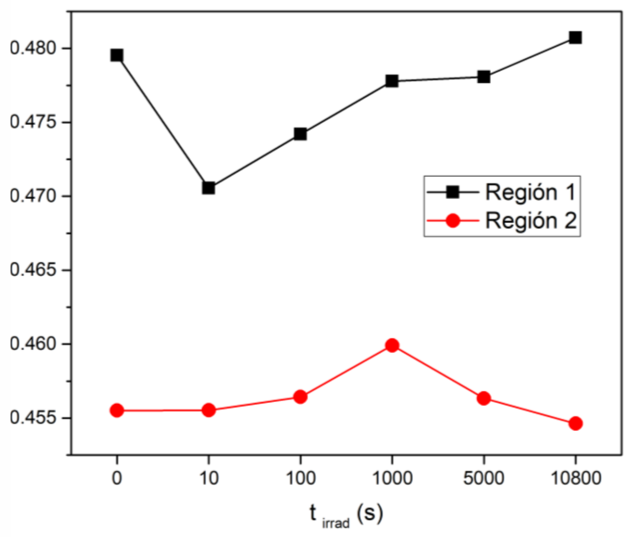
Region 1



Region 2



Parámetro S y t_{irrad}



- Inicialmente se forman muchas monovancias, las cuales se aglomeran y luego forman clústeres.

- Los clústeres de monovacancias se disocian formando defectos complejos Cu$-V_O^+$ o Cu$-V_{Cu}^-$.

- En la **Región 1** la concentración de las monovacancias aumenta continuamente.
- En la **Región 2**, S solo disminuye luego de 1000s sugiriendo la reducción por los que las dimensiones de los clústeres de defectos complejos y la recuperación de la red.

6. Referencias bibliográficas