Preparation and Characterization of Pure and Decorated Metal Oxide Materials for Energy Applications Using Physical Vapor Deposition Methods

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THE UNIVERSITY OF TENNESSEE KNOXVILLE

JIAM JOINT INSTITUTE FOR ADVANCED MATERIALS

Joint Institute for Advanced Materials (JIAM)

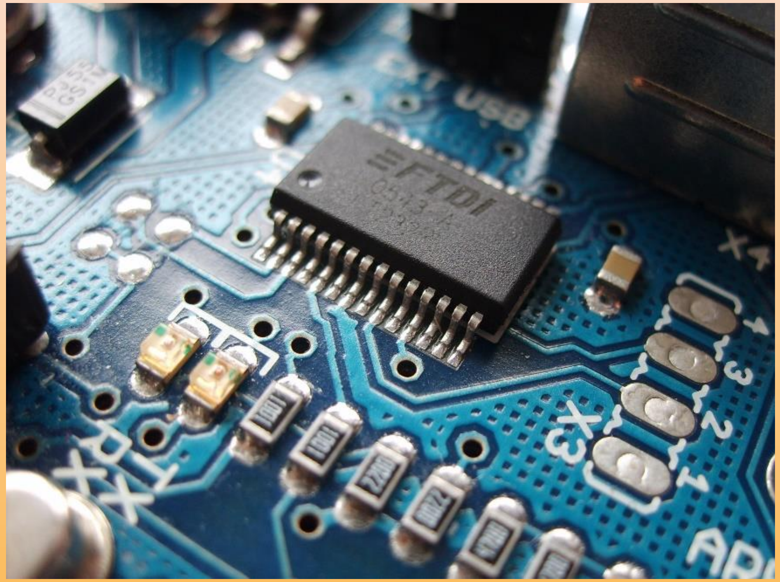
Joint Facility for Science and Engineering at the University of Tennessee, Knoxville

Spallation Neutron Source (SNS) at ORNL

Overview

- ✓ From macro to micro: the “nanoparticle revolution”
- ✓ Motivation: importance of nanomaterials in energy applications
- ✓ Metal decoration of metal oxides
  - Choice of materials
  - Experimental apparatus and methodology
- ✓ Characterization of decorated materials: evidence of metal deposits
- ✓ Future prospects of our work
- ✓ Deposition methods for cavities applications @Fermilab

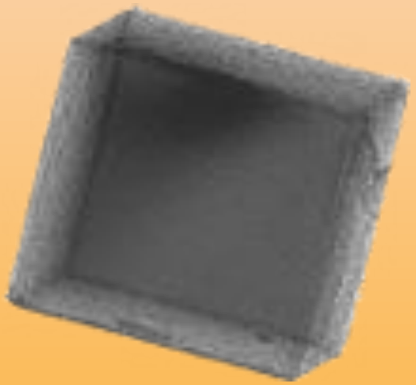
Materials are everywhere



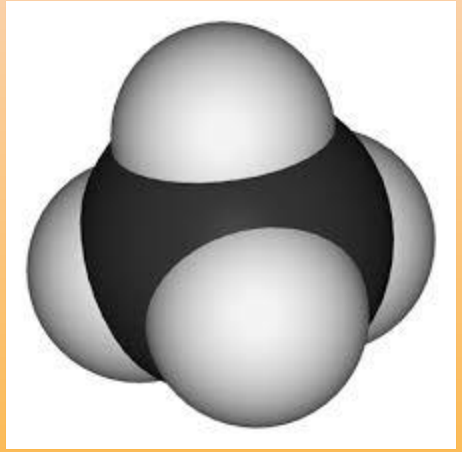
https://td.fnal.gov/

From macroscopic materials to nanoparticles: advent of new properties

1 m



200 nm



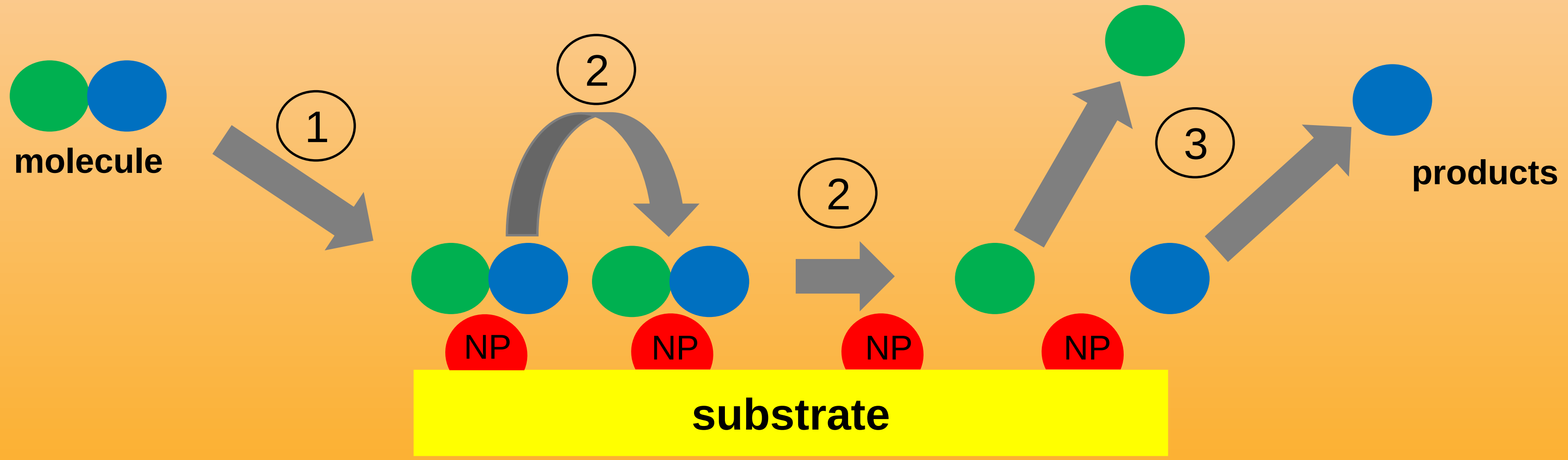
5 Å

NEW OR DIFFERENT PROPERTIES ARISE

- Different (enhanced) response to external fields
- Enlarged surface area (increased surface-to-volume ratio)
- Chemical activity (catalysis, energy conversion, …)

Heterogeneous catalysis: nanoparticles in action

Catalysis: improve the efficiency of a certain chemical reaction
Heterogeneous: catalyzer and chemical species taking part to the reaction of interest are in different phases (e.g. **gas** phase reaction on a **solid** substrate)



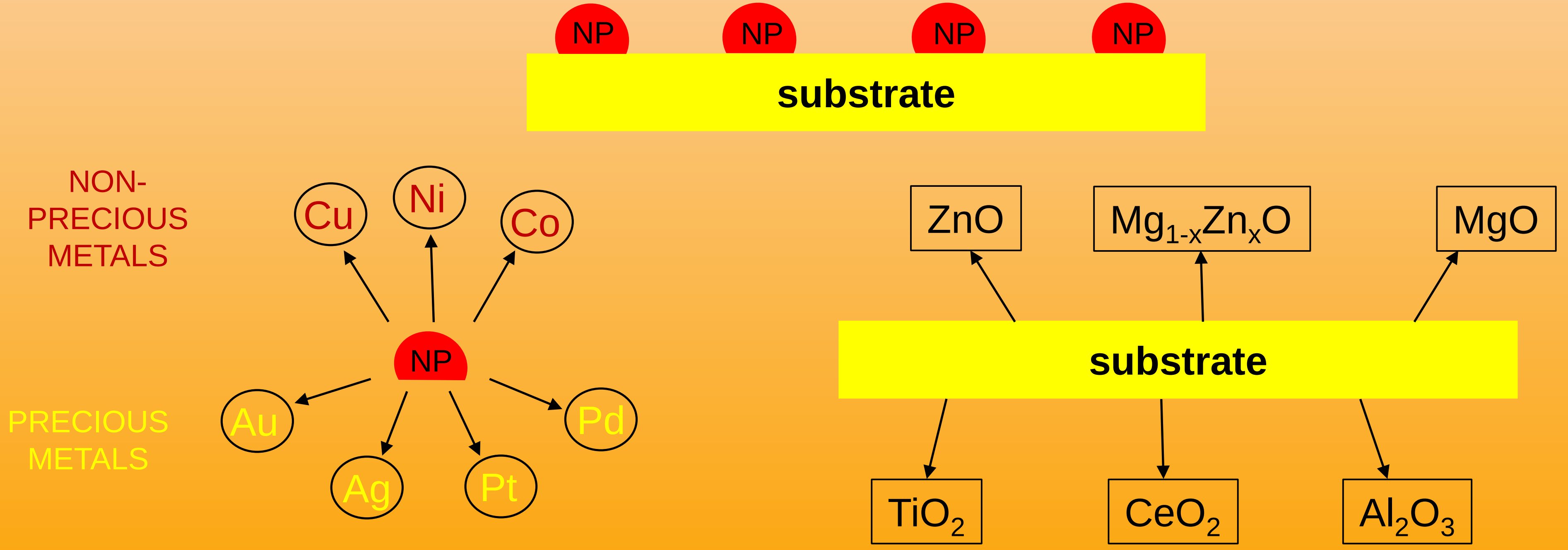
1) **ADSORPTION** TO THE SURFACE

2) MOLECULE **DISSOCIATION/REACTION** WITH OTHER SPECIES

3) **DESORPTION** FROM THE SURFACE

Certain substrates are good for certain reactions

- In heterogeneous catalysis, **efficiency** and **rates of chemical reactions** (i.e. yield of certain products from a set of certain reagents) are enhanced by the activity of a solid substrate
- A material (insulator or semiconductor) can act as a **support for deposits of small metallic particles**

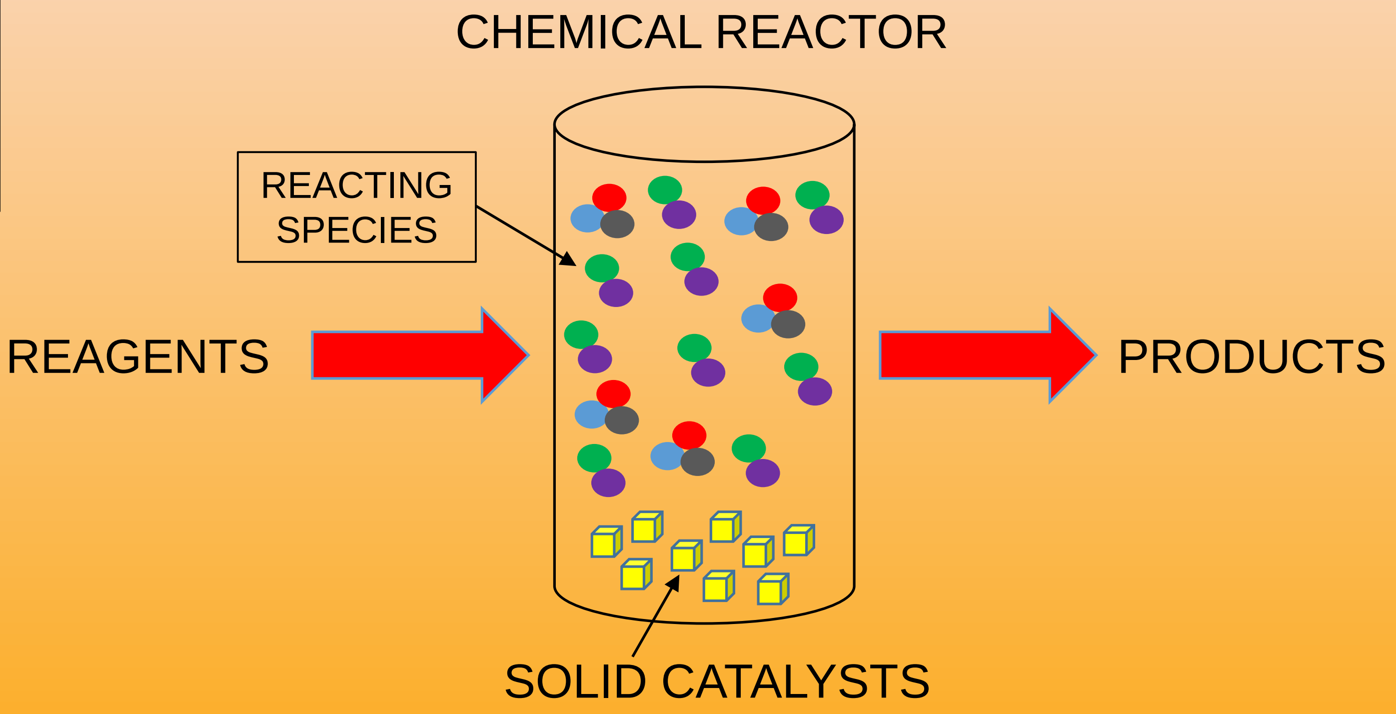


SUBSTRATES: POWDERS TO ENLARGE SURFACE AREA EXPOSED TO REAGENTS

- Scientists discovered the **catalytic properties of precious metals** (Au, Ag, Pt, Pd) about 50 years ago: think about Pd in your car's **catalytic converter**
- **Metal oxides** (typically insulators) turn out to be very suitable supports
- Deposition methods are both **chemical** (wet synthesis) and **physical** (dry synthesis)

Chemistry for energy harvesting and conversion

Reagents are in the gas phase and flow on a bed of catalytic particles



Products are obtained from reagents-catalysts interaction (can be liquid)

- Some reactions are of very high interest to **industrial processes**
- Nowadays energy challenges: conversion of **natural feedstock** into **usable resources**
- Conversion of **methane** gas (CH_4) into the solvent **methanol** (CH_3OH)

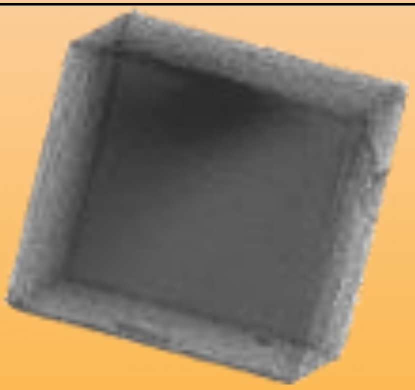
Our project: research goals

- We can produce **high-quality size-selected metal oxide nanoparticles**.
- We want to develop a **deposition method that bypasses the use of chemicals**, in order to maintain the **purity of our substrates**.
- We want to **study** the fundamental (and then applied) **properties of the novel materials**.

Metal oxides: preferred choice for support

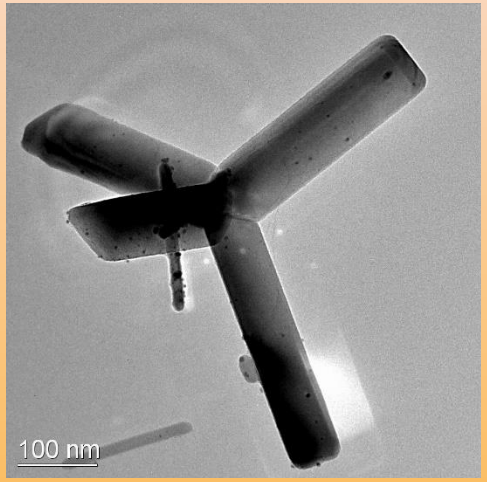
Metal oxides (MO) offer a broad range of electronic properties, spanning from large bandgap insulators (MgO) to wide bandgap semiconductors (ZnO)

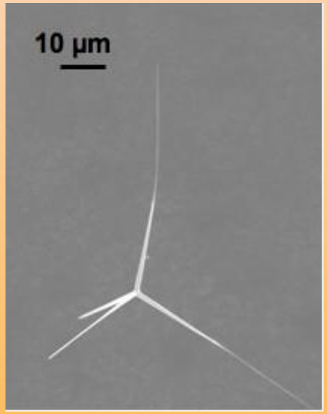
MgO

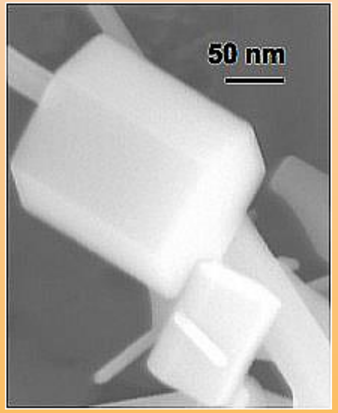


TEM image of MgO nanocube (courtesy of Larese Group)

ZnO







TEM images of different ZnO morphologies (courtesy of Larese Group)

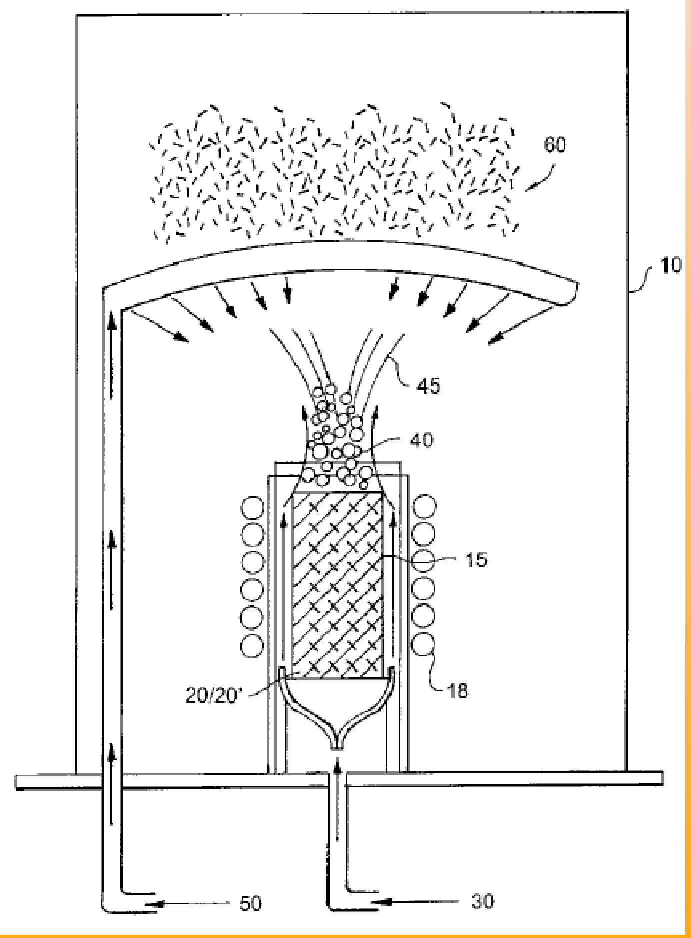
<u>Our group is strongly interested in studying both fundamental and applied properties of MO</u>

Why are MO interesting?

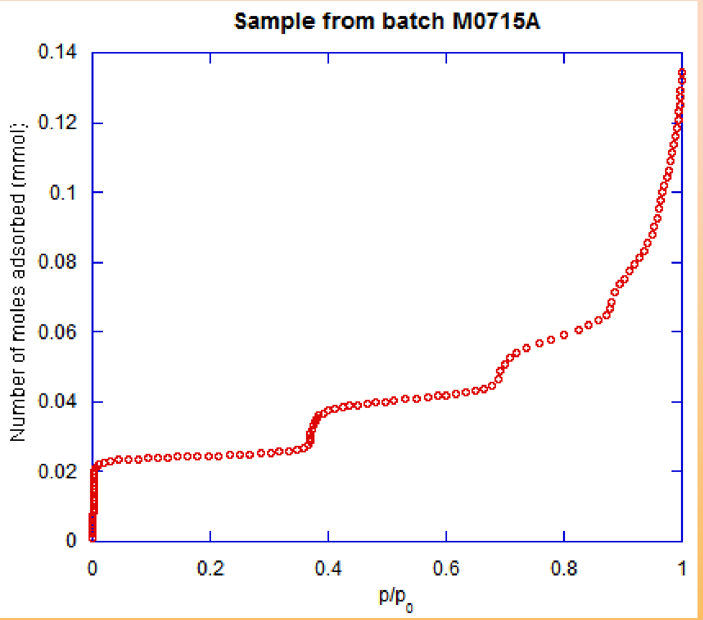
- Crystal structure: simple cubic for MgO, wurtzite (hexagonal) for ZnO
- Simple structures: defects at the surface, e.g. vacancies, color centers, interstitials
- Preferential orientation of the nanostructures, e.g. MgO(100) facets, suitable for deposition
- Easy and cheap to synthesize in powdered form (improving surface area properties)

Metal oxides: vapor entrainment

Synthesis conditions (e.g. gas flow, induction furnace heat) will determine narrow size distribution of oxide nanoparticles



Schematic of vapor entrainment-based synthesis apparatus



MgO characterization with methane gas adsorption (at 77 K): multi-step feature helps determination of material's quality (purification with H.T. at 950 °C)

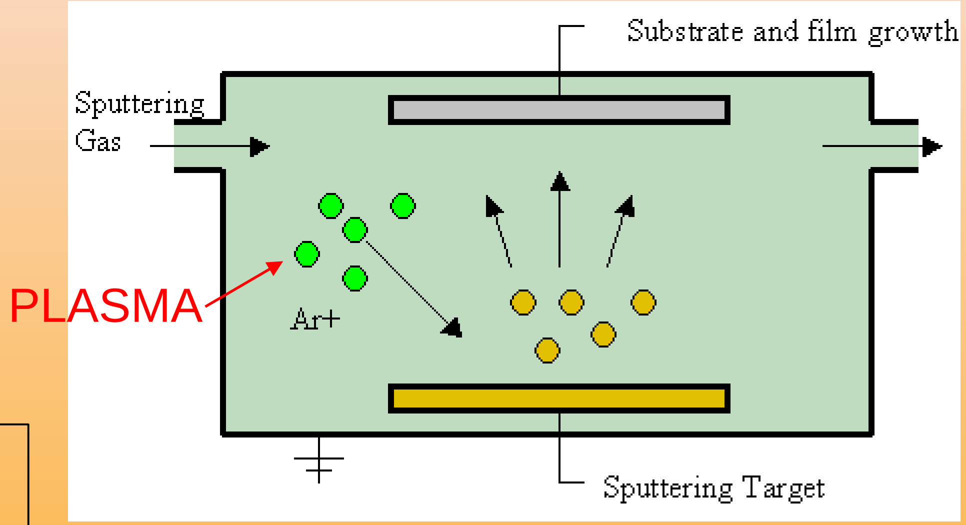
- In-house synthesis of MgO and ZnO
- Potentially any metal oxide synthesis starting from pure metal

Kunnmann, W. and Larese, J.Z., U.S. Patent No. 6,179,897 B1 (2001).
Mursic, Z., Lee, M.Y.M., Johnson, D.E., and Larese, J.Z., *Rev. Sci. Instrum.* 67, 1886 (1996).

The deposition process: sputtering

Physical vapor deposition (PVD) avoids the use of chemical agents in delivering pure species (atoms, clusters) onto a substrate

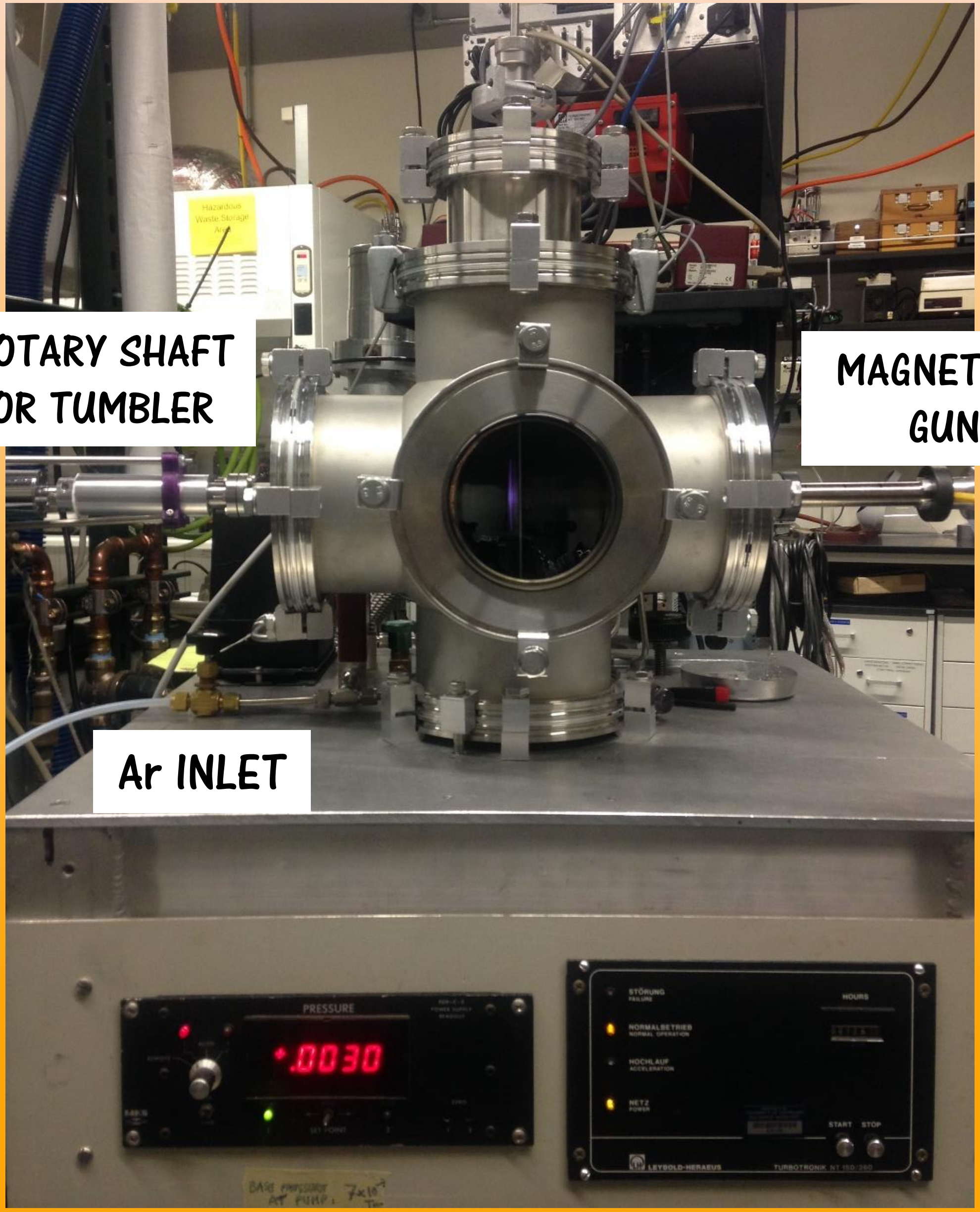
Example: contamination of **MgO** by **acetone** and etching of surfaces when solvent-based deposition methods are used

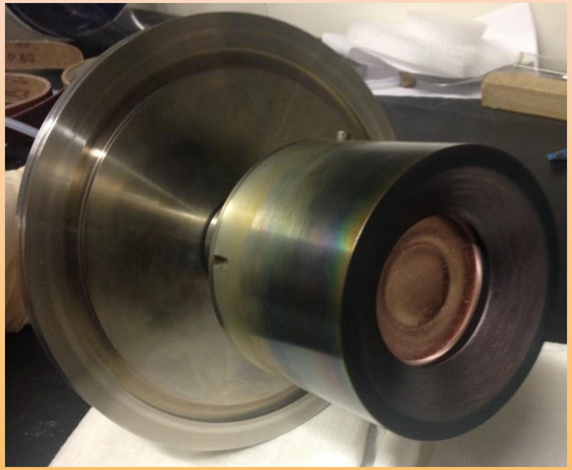


Sputtering as a PVD method can help deposition of pure metal clusters on clean MO surfaces, providing an opportunity to study the fundamental properties of the new combined material

- Cleanliness and purity of surfaces: more insightful study of **surface mediated chemical reactions** that can happen on the composite materials (initial driving force for the project)
- **Modification** of the electronic structure/**Addition** of new properties to the starting material (or vice versa)
- **Non-precious transition metals**: complex electronic structure is not fully understood yet
- Great candidates to **explore** a new deposition methodology (conveniently available)
- **Copper** (non-magnetic), **nickel**, **cobalt** (magnetic)
- Given choice of metal species, deposition will mostly depend on **effusive flux** and **sticking coefficient** on the surface

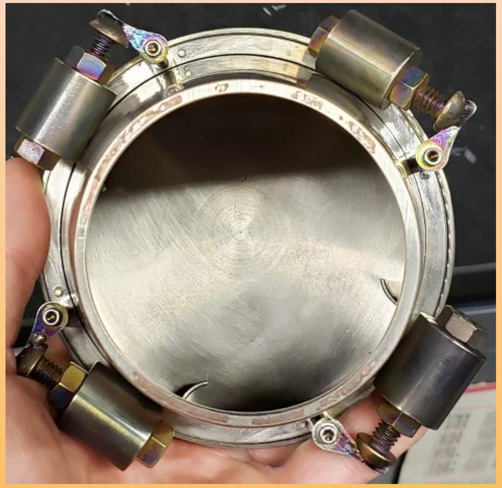
The deposition apparatus



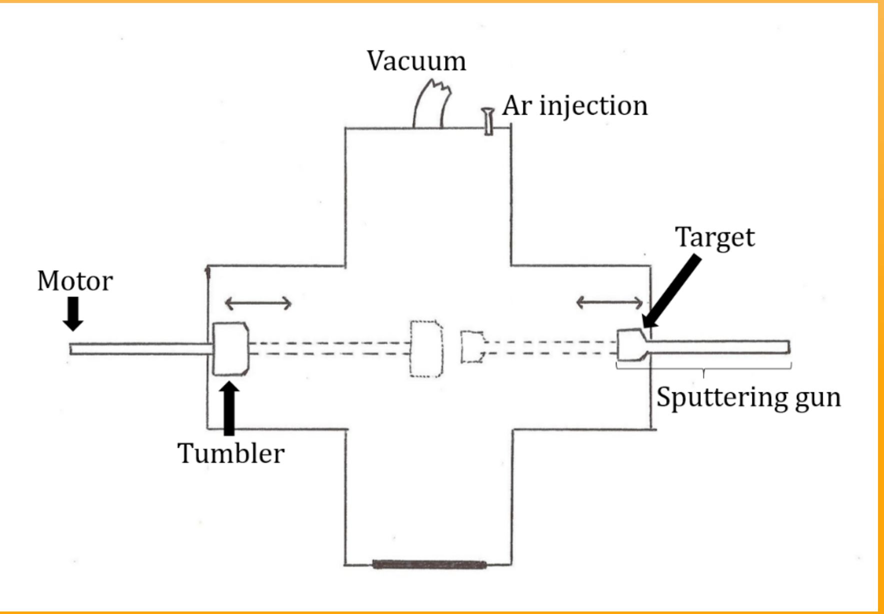


MAGNETRON SPUTTERING GUN

TUMBLER WITH TAPPING WEIGHTS



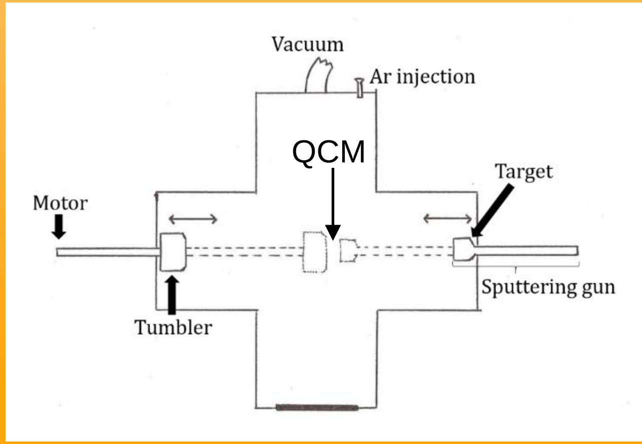
DEPOSITION CHAMBER SCHEMATIC

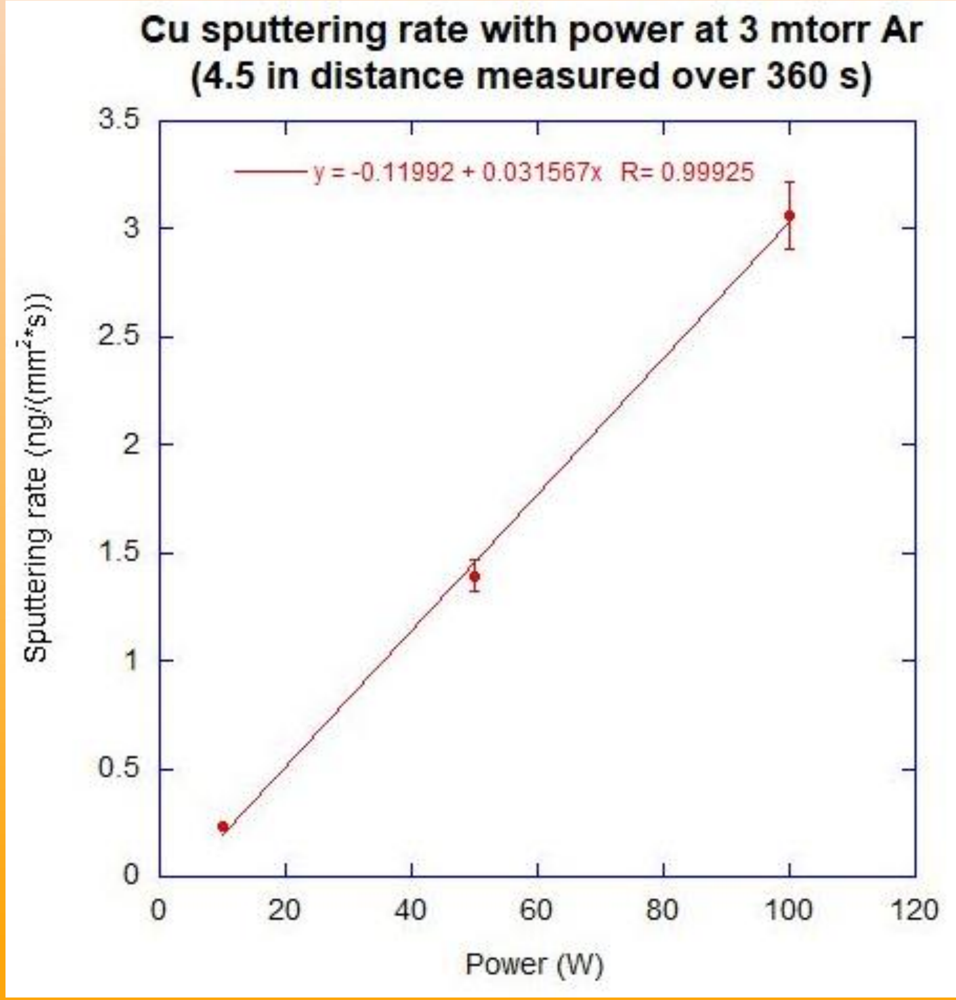


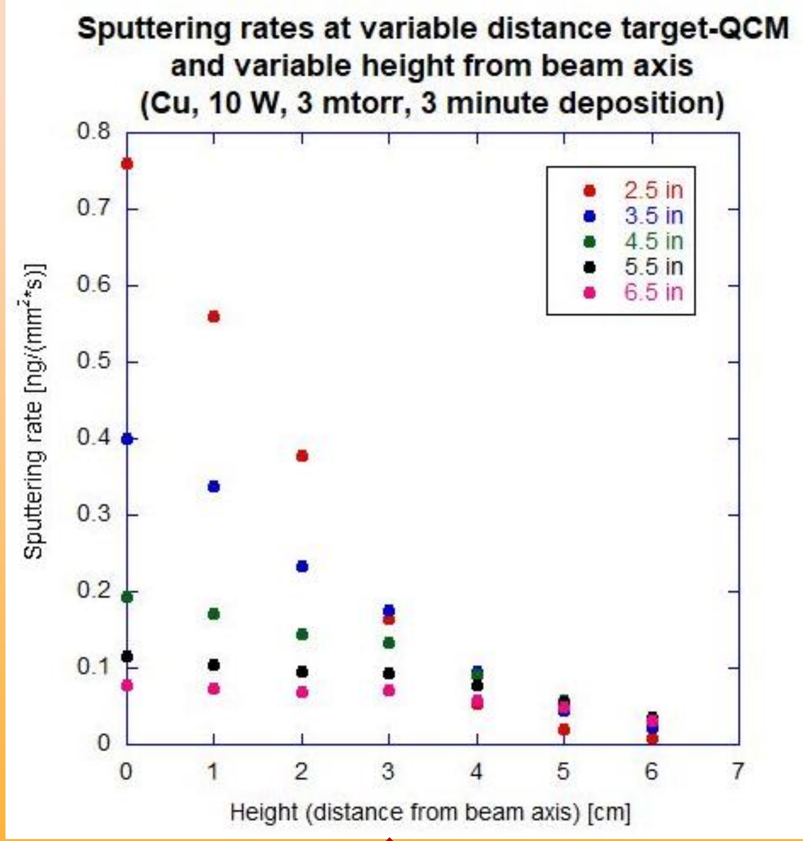
QCM

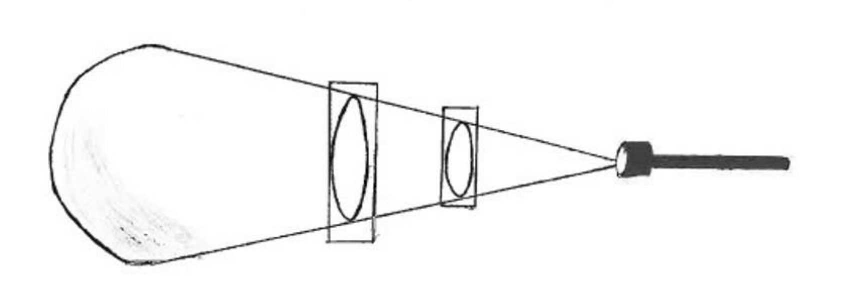
Calibration of the beam

Quartz Crystal Microbalance (**QCM**): piezoelectric crystal that resonates upon application of AC voltage







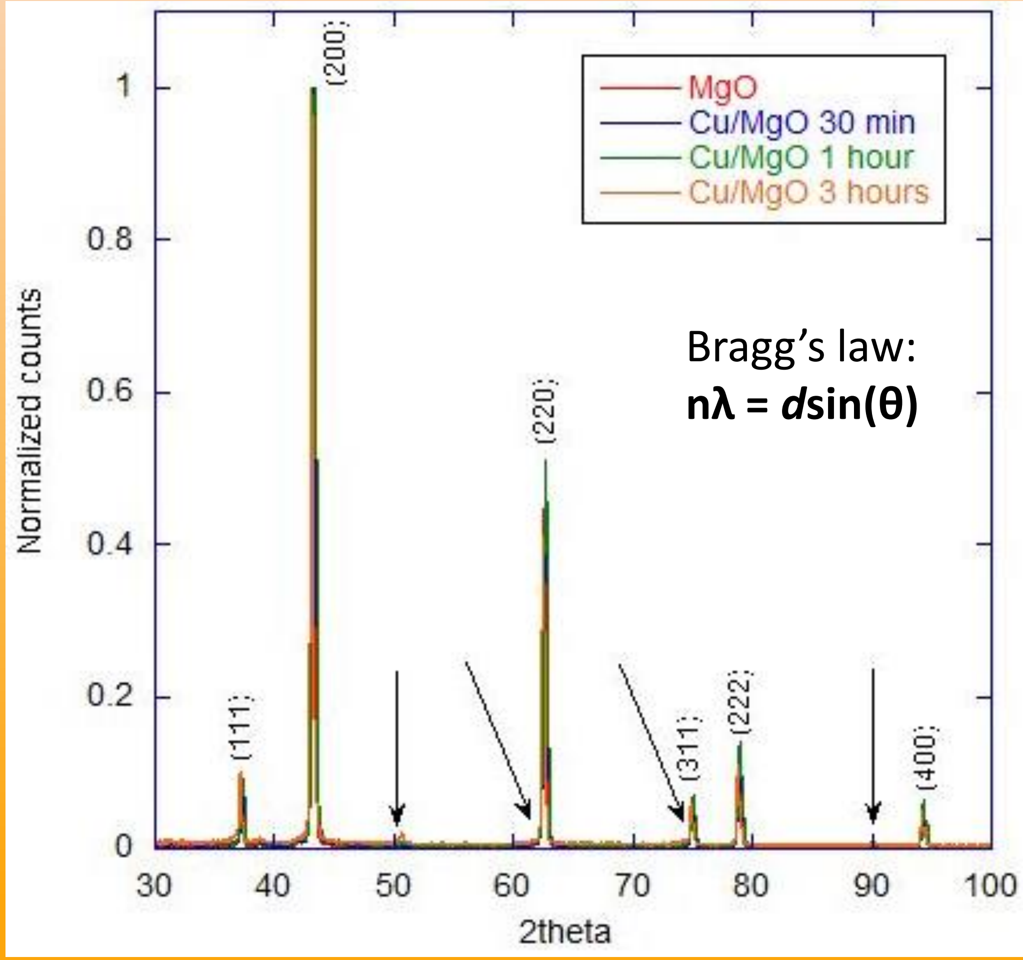


QCM sensitivity:
0.124 ng/(mm^2·Hz)

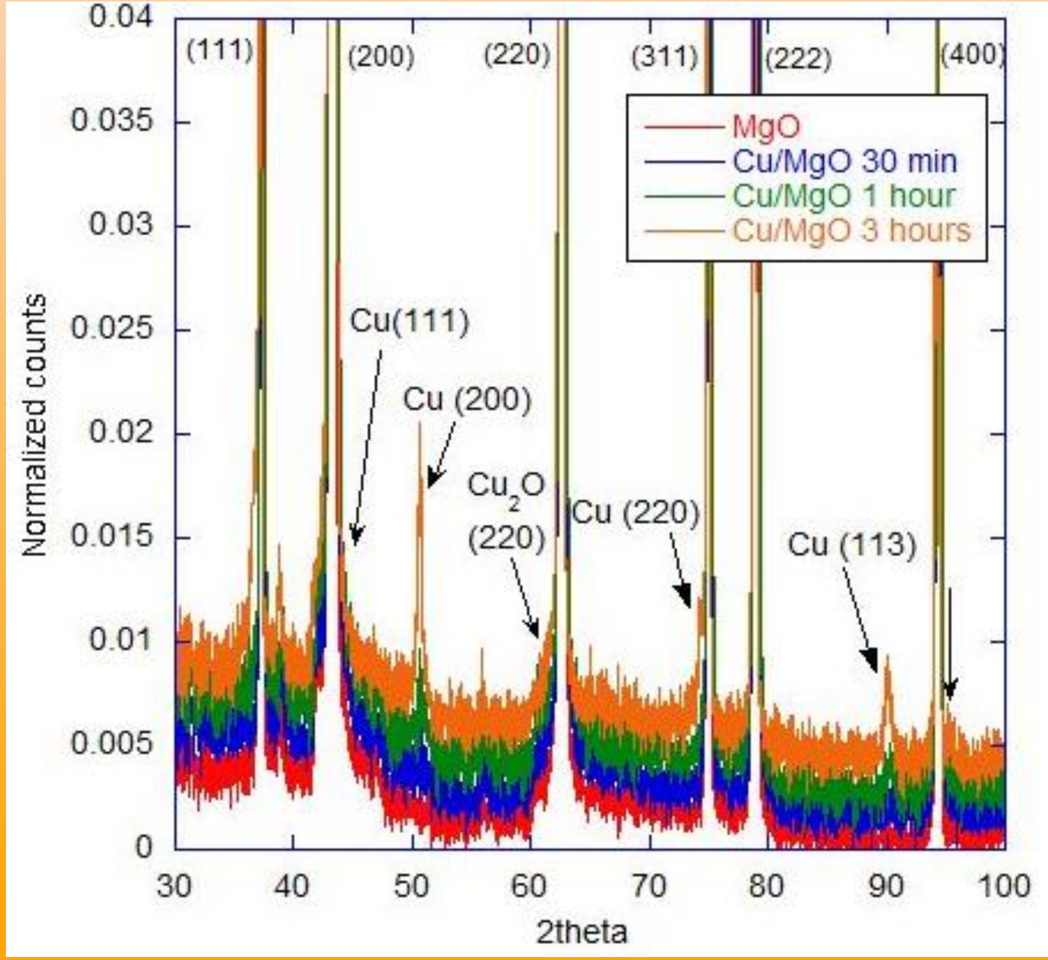
Sputtering rate (10 W power):
0.230 ng/(mm^2·s)

Structural investigation of Cu/MgO

Powder X-ray diffraction pattern (XRD) of pure and Cu/MgO



Details at low intensity of Bragg reflection

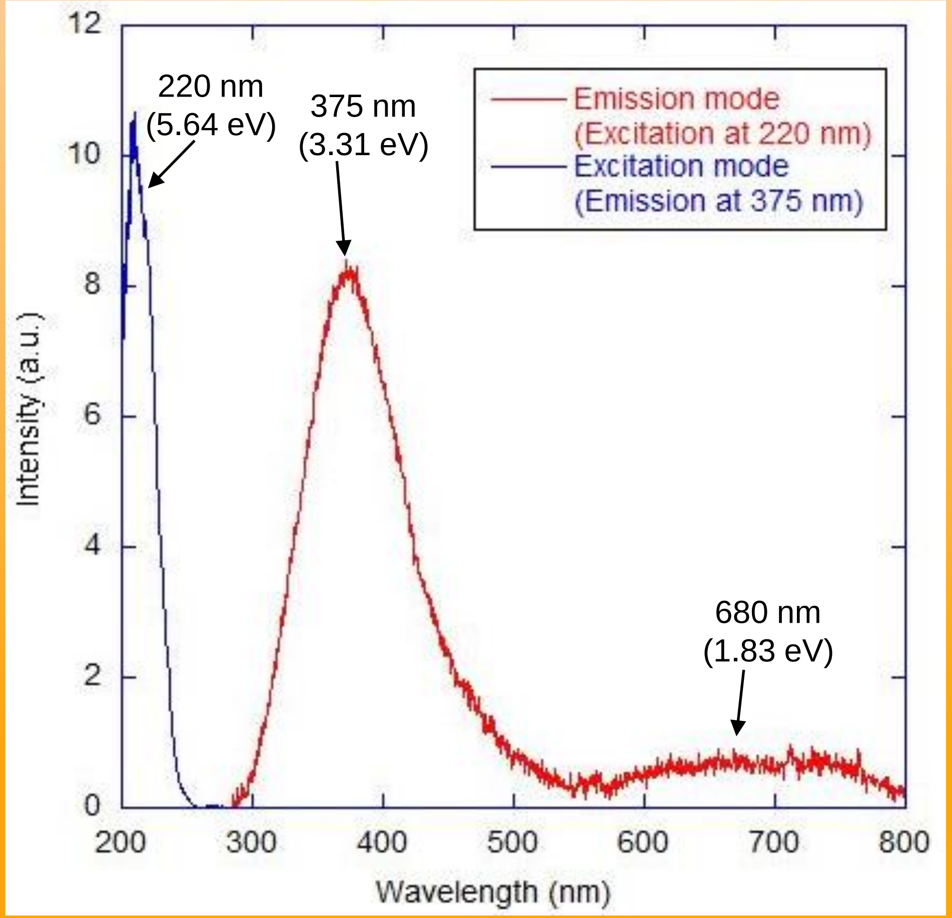


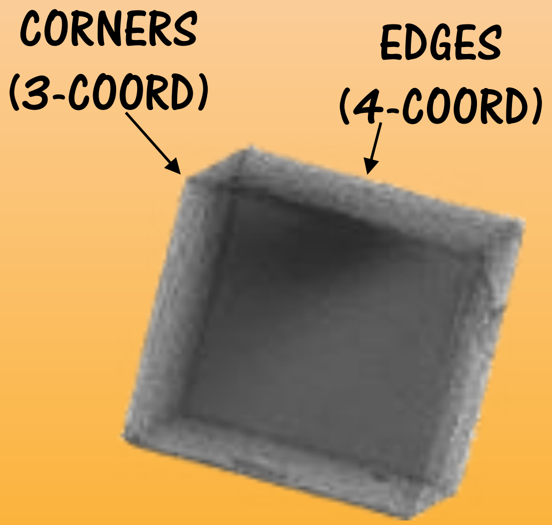
- Copper and Cu-oxides deposits appear in crystalline form on the MgO with increasing deposition time
- The question is: how do these clusters of the metal adhere to the MO surface?

Optical probe: photoluminescence

- We are interested in learning more about the optical properties of pure and decorated MgO
- Photoluminescence (PL) measured an emitted spectrum upon excitation of a material with UV-Visible light
- Insulator: no excitation of band gap, rather of **surface states**

PL EXCITATION AND EMISSION SPECTRA





Purity of our MgO allows for low surface defect concentration

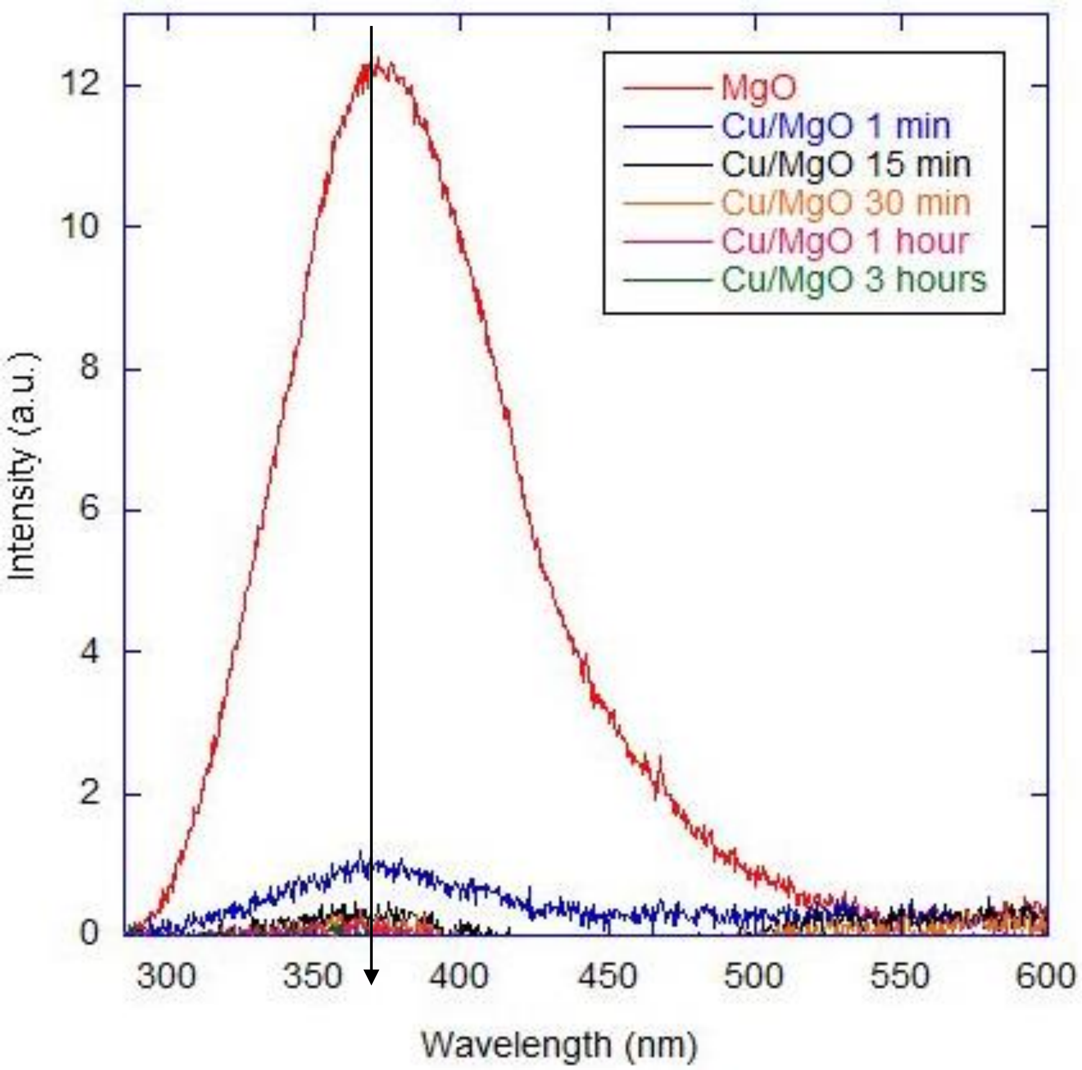
Edges and corners of the nanocubes constitute the majority of the emitting sites (edges being in far greater number)

- 5.64 eV: excitation of more strongly bound sites (4-coordinated) emitting at 3.31 eV
- Much reduced contribution from lower-coordination sites (very weak emission at ~1.83 eV)
- Focus on main emission band

Coluccia et al., *J. Chem. Soc., Faraday Trans. 1*, **75**, 1769-1779 (1979); Shluger et al., *Phys. Rev. B* **59**, 3 (1999) 2417-2430; Stankic et al., *Angew. Chem. Int. Ed.* **2005**, 44, 4917-4920.

Cu/MgO: quenching of PL

ELECTRONIC STRUCTURE AT THE SURFACE CHANGES DUE TO PRESENCE OF METAL DEPOSITS

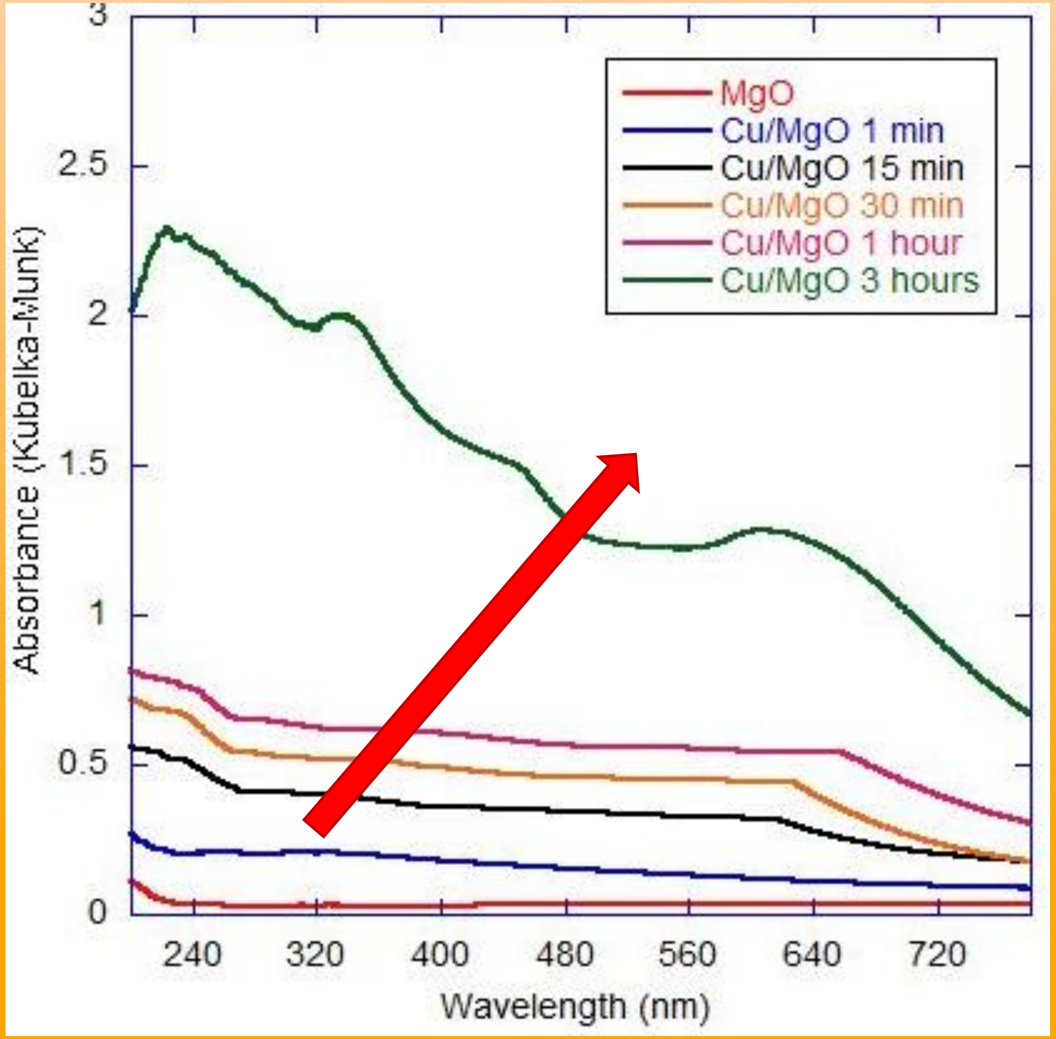


- A new material with different coloration is produced after deposition
- Increasing deposition time **progressively quenches** the main PL emission feature
- PXRD data suggests presence of metal species on the major emitting sites
- Post-deposition H.T. does not seem to influence PL quenching differently (processes do not affect new structure, e.g. **reduction**)

Top left: As-deposited Cu/MgO
Top right: Cu/MgO H.T. 500 °C
Bottom left: Cu/MgO H.T. 950 °C
Bottom right: Cu/MgO H.T. 950 °C (improved deposition w/"tapping" weights)

Measuring the absorbance of Cu/MgO

ABSORPTION OF LIGHT IN THE UV-VIS SPECTRUM OF THE COLORED MgO IS GREATER THAN PURE MgO



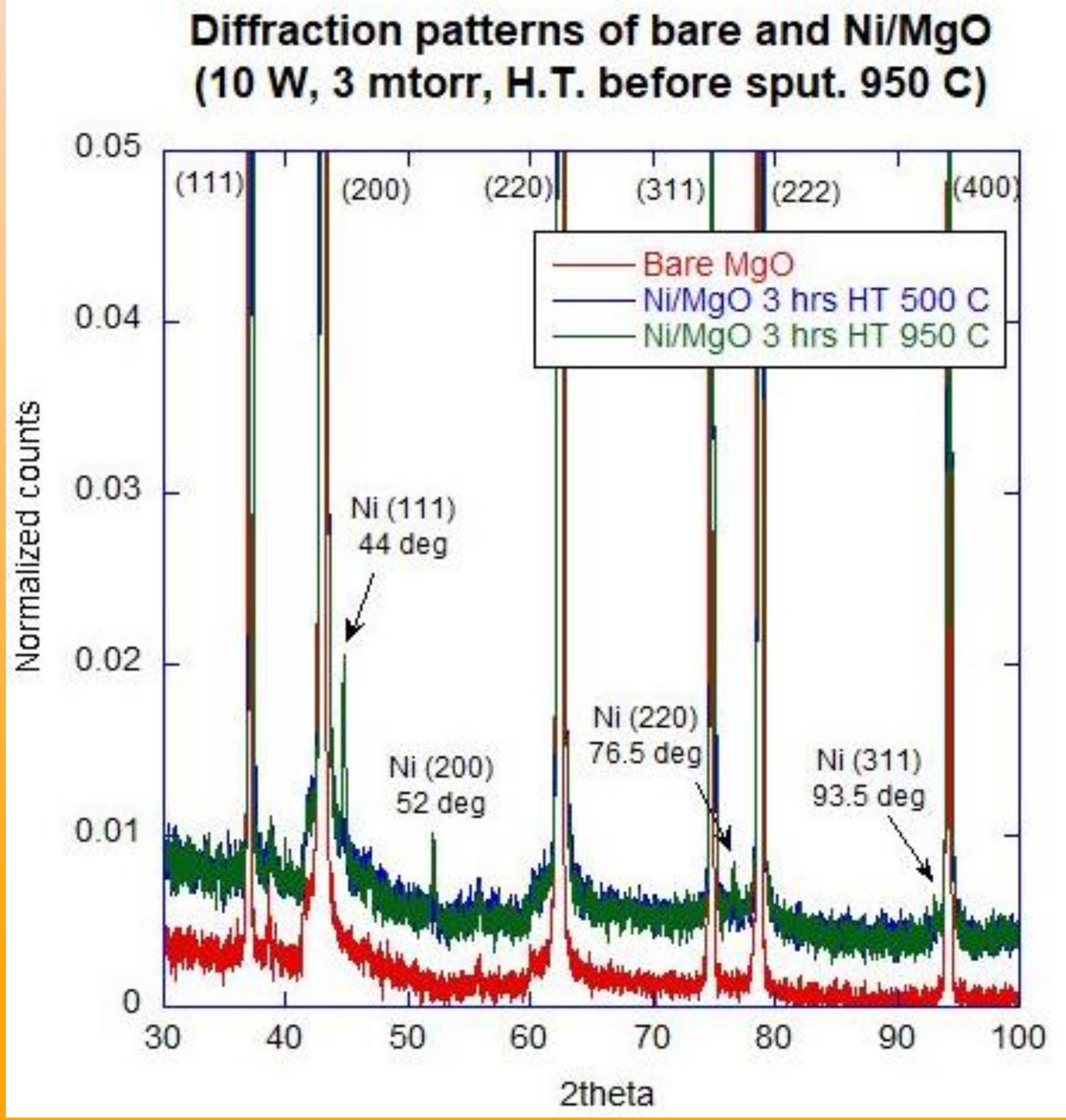
- Absorbance calculated from diffuse reflectance using the **Kubelka-Munk** function:

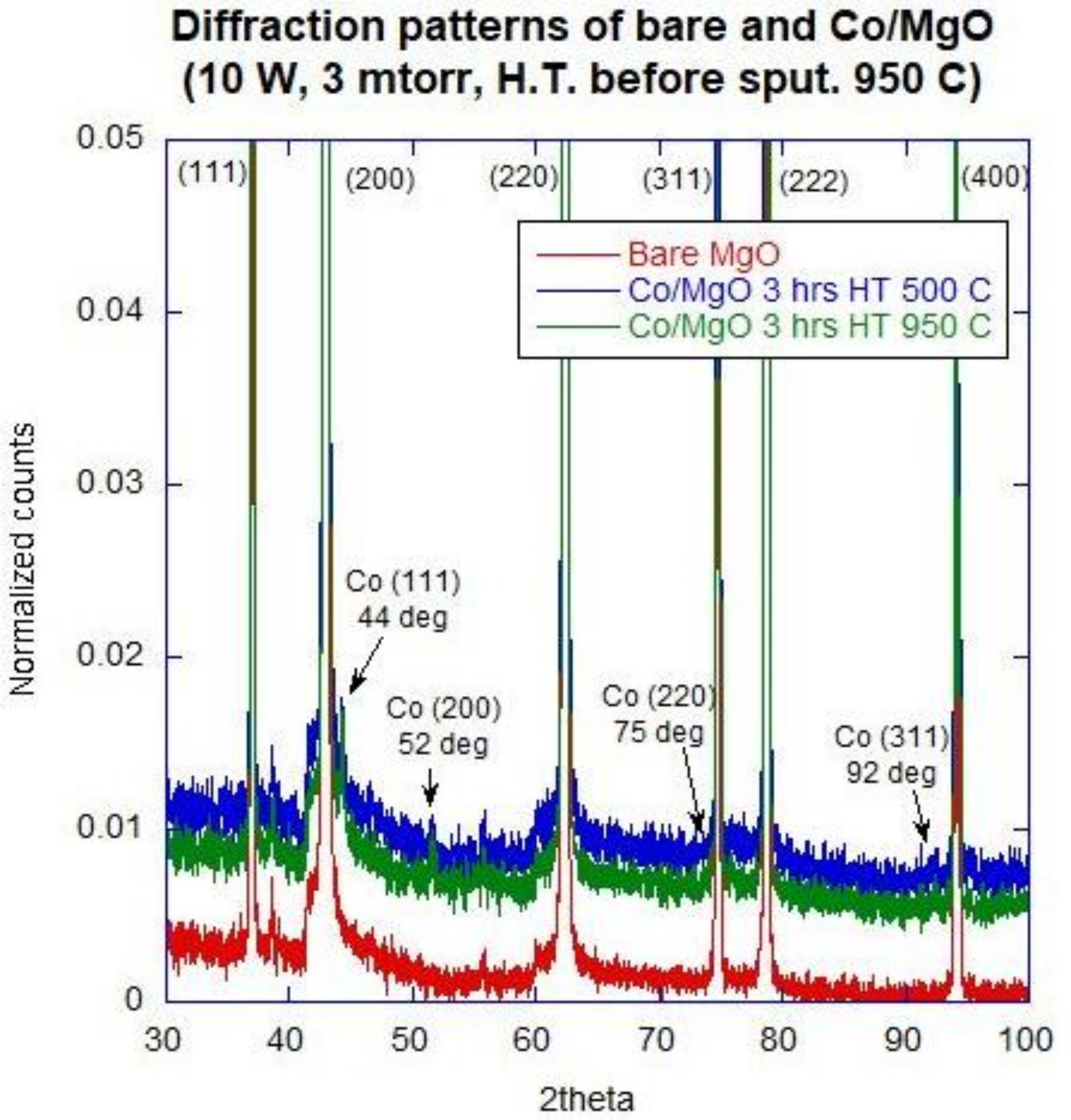
$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s}$$

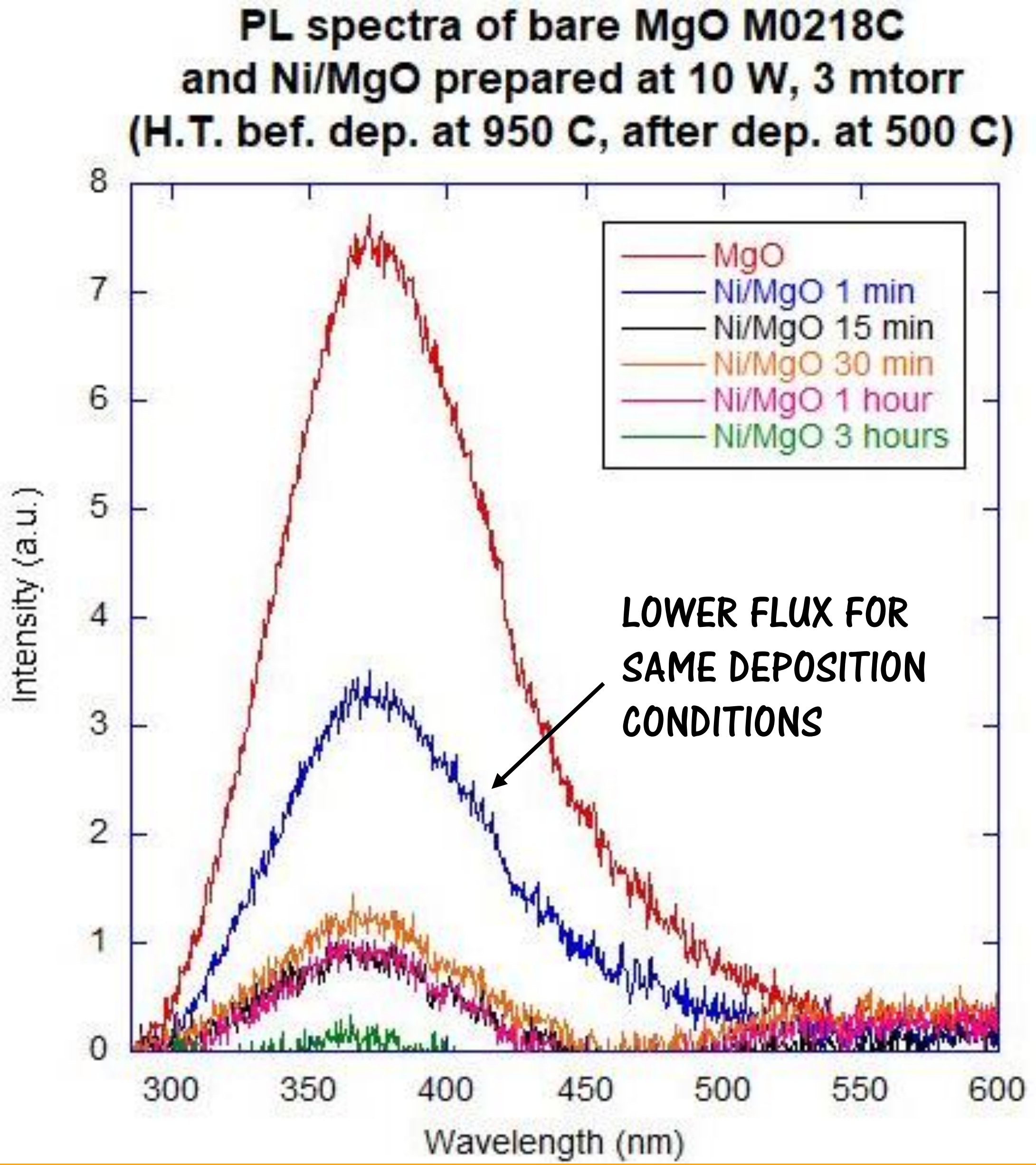
- R_∞ refers to (completely) absorbing and reflecting standards; k and s are the absorption and scattering coefficients, respectively
- Scattering (from particles) assumed equal (“infinitely” thick sample), **reducing $F(R_\infty)$ to absorption from sample**
- Longest deposition time case: metal structures are responsible for absorption peaks (confirmed by PXRD)
- Difficult to uniquely assign absorbance peaks to reduced metal and/or its oxidized states

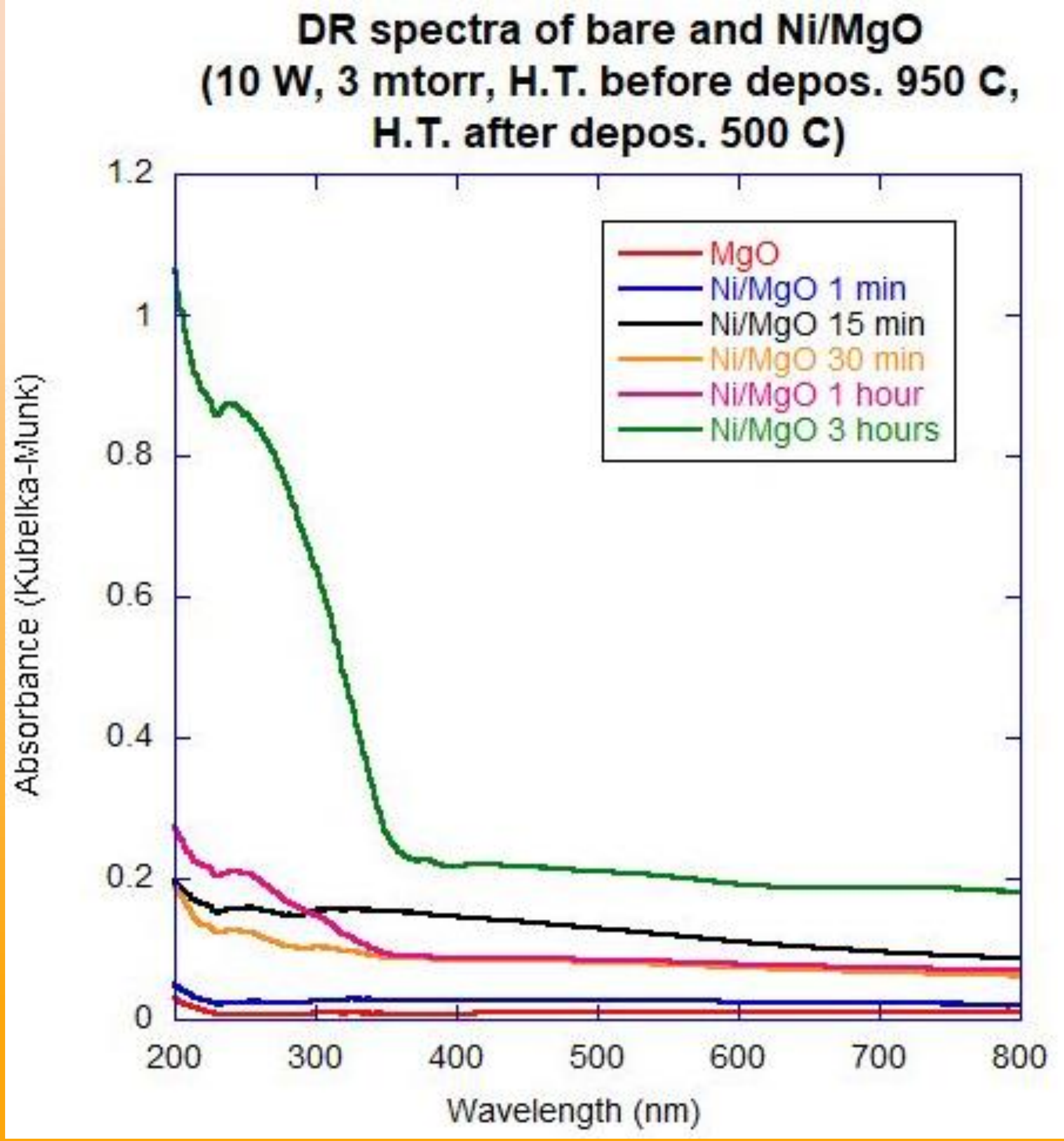
Tandon, S.P., and Gupta, J.P., *Phys. Stat. Sol.* **37**, 43 (1970); Pestryakov et al., *Chem. Phys. Lett.* 385 (2004) 173-176.

The cases Ni/MgO and Co/MgO






PL spectra of bare MgO M0218C
and Ni/MgO prepared at 10 W, 3 mtorr
(H.T. bef. dep. at 950 C, after dep. at 500 C)
MgO
Ni/MgO 1 min
Ni/MgO 15 min
Ni/MgO 30 min
Ni/MgO 1 hour
Ni/MgO 3 hours
LOWER FLUX FOR SAME DEPOSITION CONDITIONS
Intensity (a.u.)
Wavelength (nm)
0
1
2
3
4
5
6
7
8
300
350
400
450
500
550
600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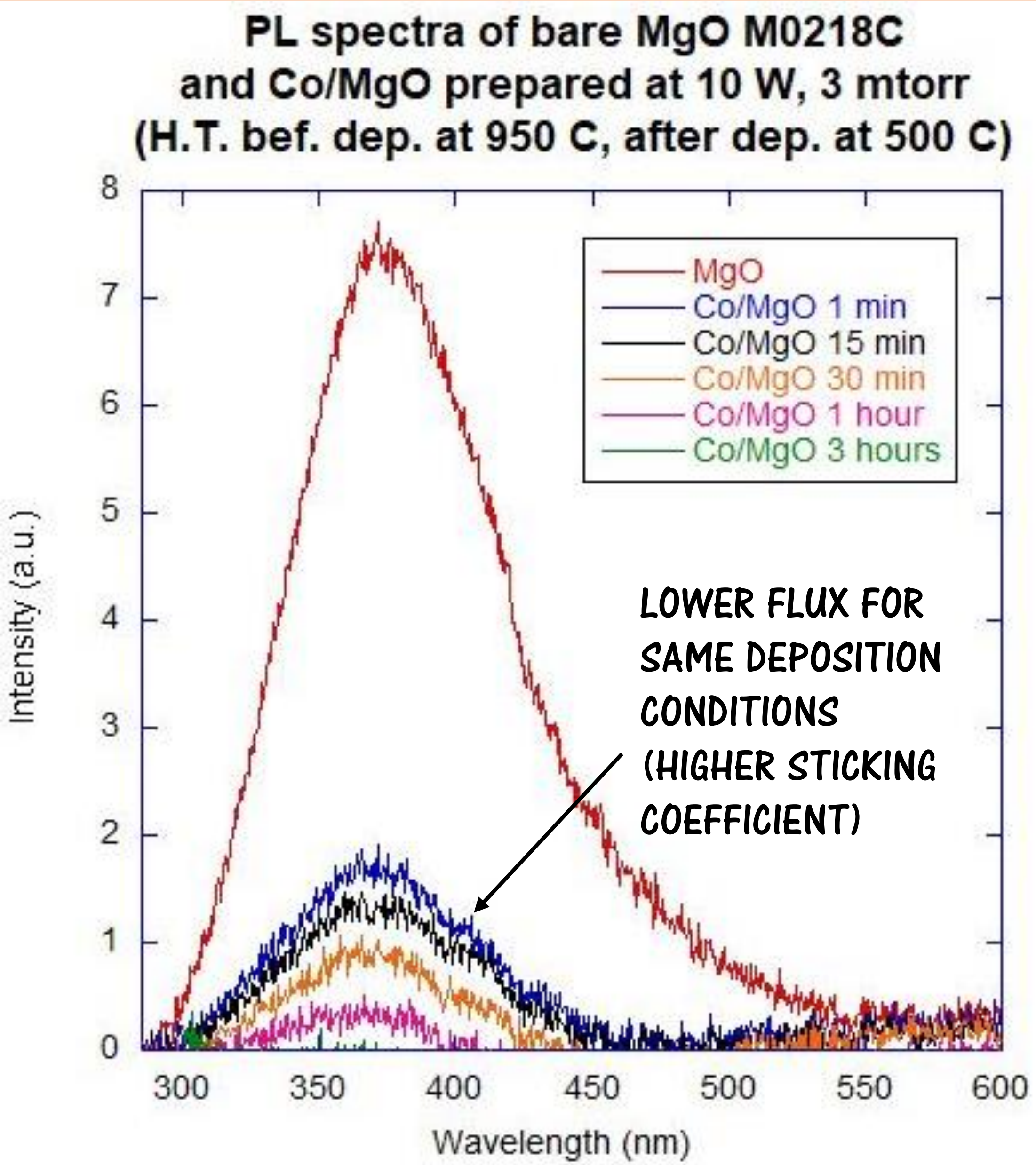
MgO
Ni/MgO 1 min
Ni/MgO 15 min
Ni/MgO 30 min
Ni/MgO 1 hour
Ni/MgO 3 hours
Absorbance (Kubelka-Munk)
Wavelength (nm)
0
0.2
0.4
0.6
0.8
1
1.2
200
300
400
500
600
700
800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MgO
Co/MgO 1 min
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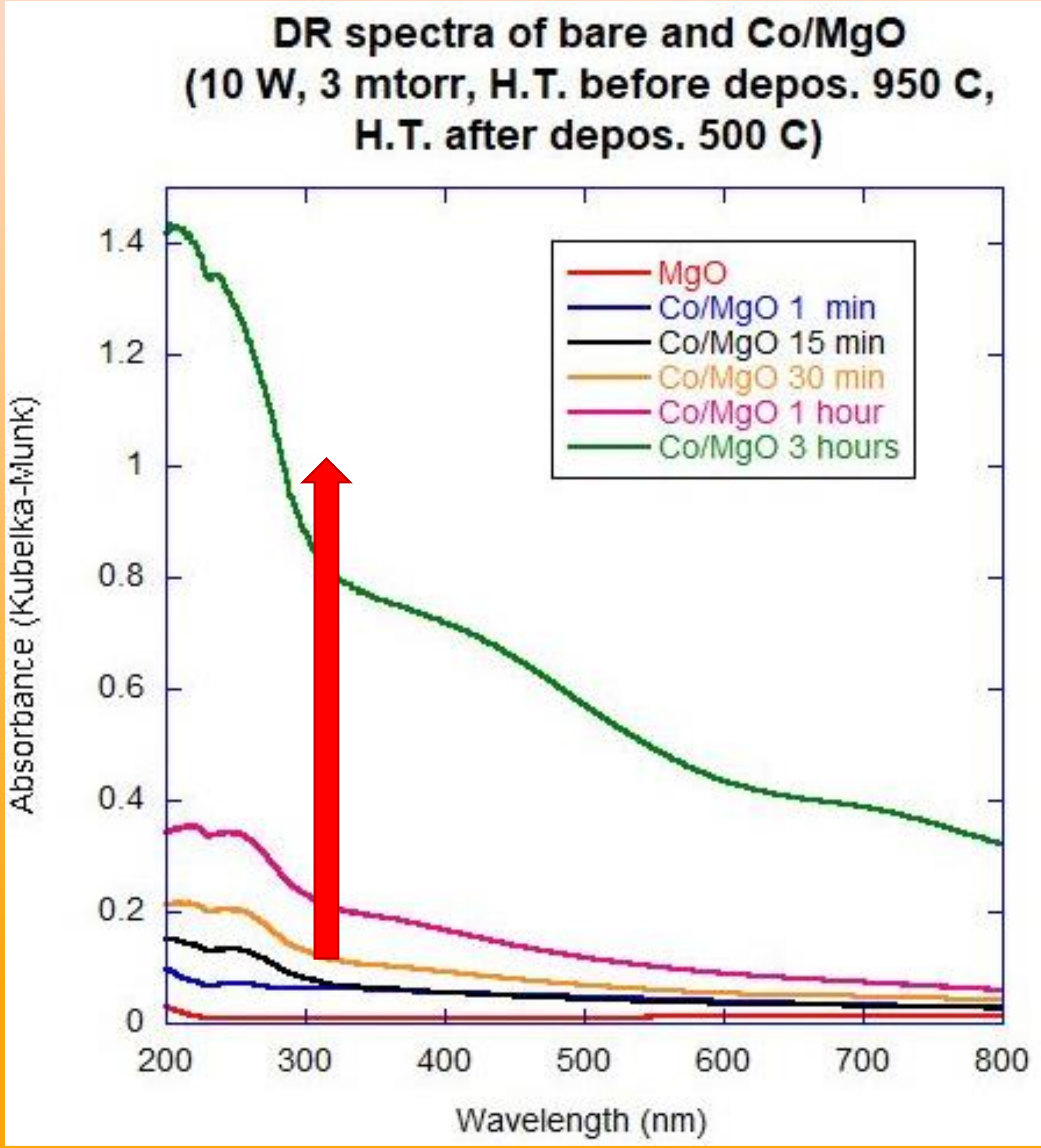
Co/MgO 30 min
Co/MgO 1 hour
Co/MgO 3 hours
LOWER FLUX FOR SAME DEPOSITION CONDITIONS (HIGHER STICKING COEFFICIENT)
Intensity (a.u.)
Wavelength (nm)
0
1
2
3
4
5
6
7
8
300
350
400
450
500
550
600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MgO
Co/MgO 1 min
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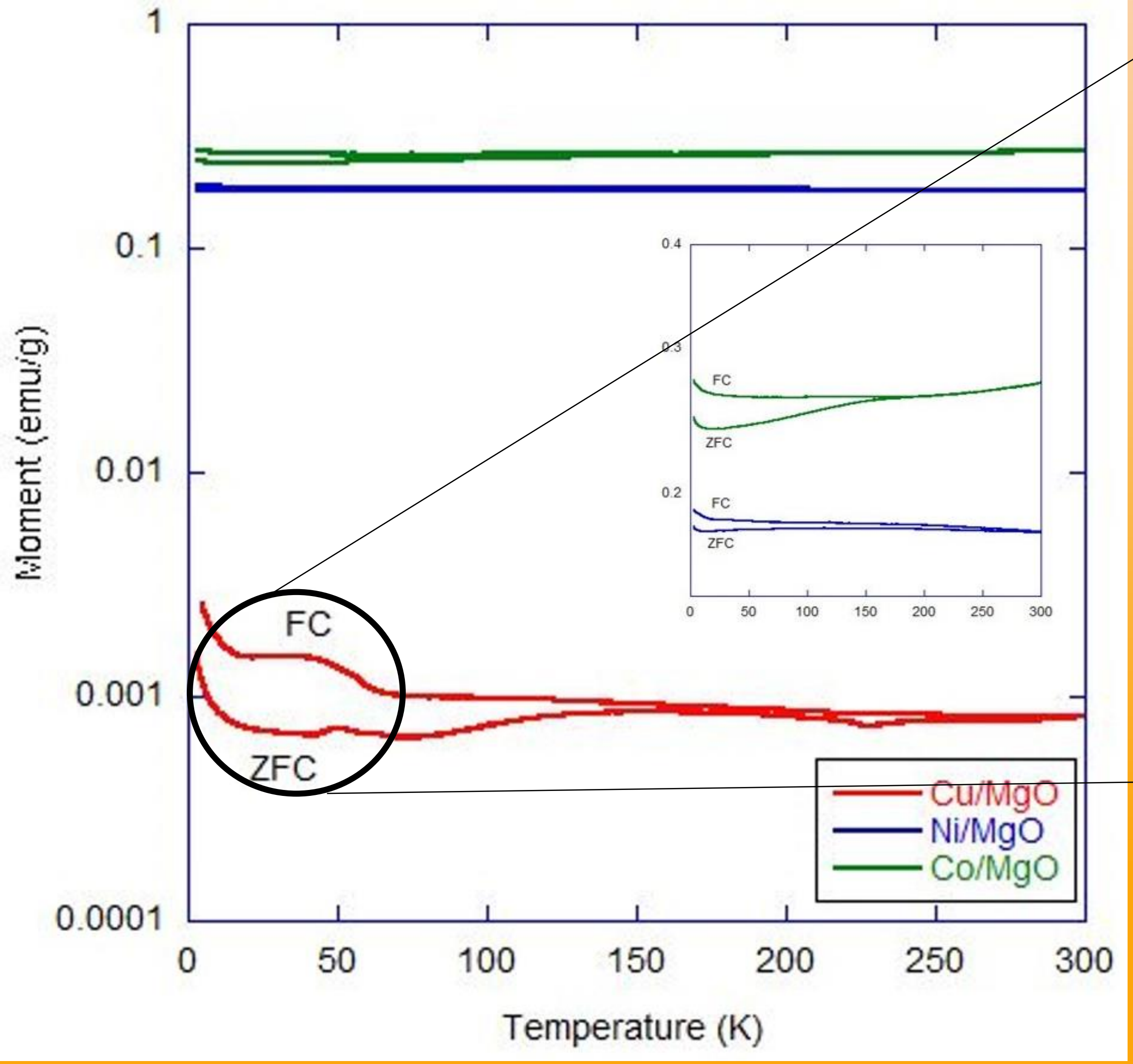
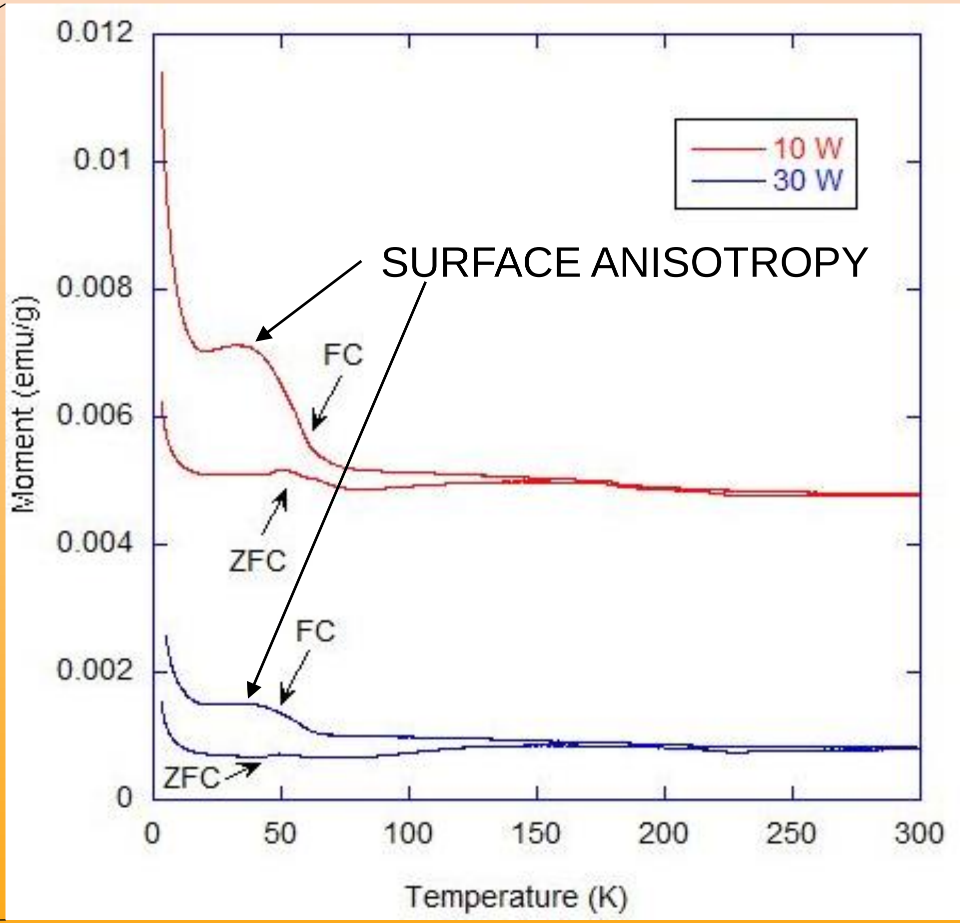
Co/MgO 30 min
Co/MgO 1 hour
Co/MgO 3 hours
Absorbance (Kubelka-Munk)
Wavelength (nm)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
200
300
400
500
600
700
800

SQUID: Cu/MgO vs. Ni,Co/MgO

MAGNETIC MOMENT OF THE DECORATED MgO PARTICLES
IN RESPONSE TO EXTERNAL MAGNETIC FIELD



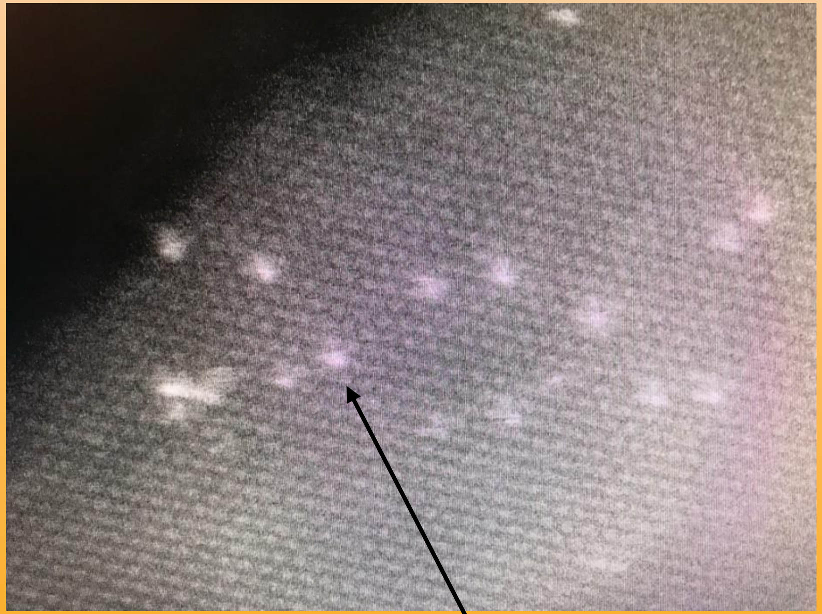


- Possible presence of small Cu_2O NPs (smaller <10 nm) experiencing surface magnetic anisotropy (high surface-to-volume ratio)
- Potential ferromagnetic character: $M(T) = \chi(T) \cdot H$?
- Superconductivity in copper-oxide materials

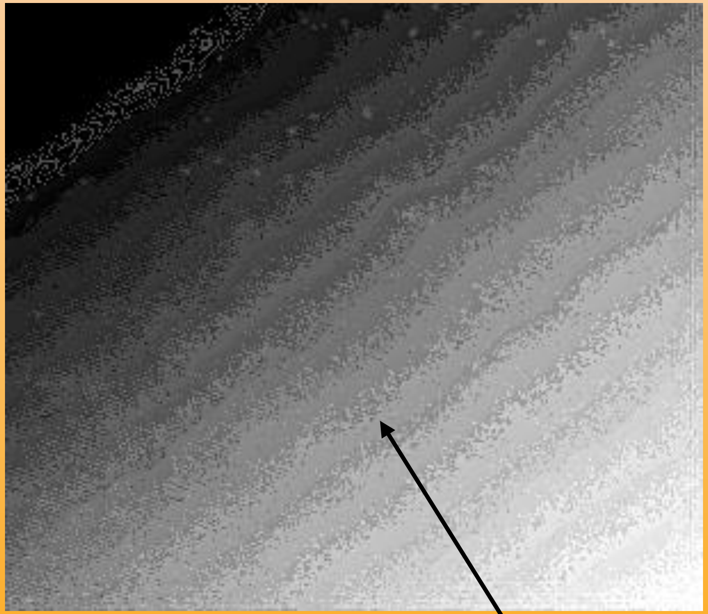
Wu et al., *Jpn. J. Appl. Phys.* **47**, 706 (2008).

Electron microscopy

Z-contrast scanning transmission electron microscopy (STEM) reveals presence of metallic clusters on the MgO(100) surfaces with atomic resolution



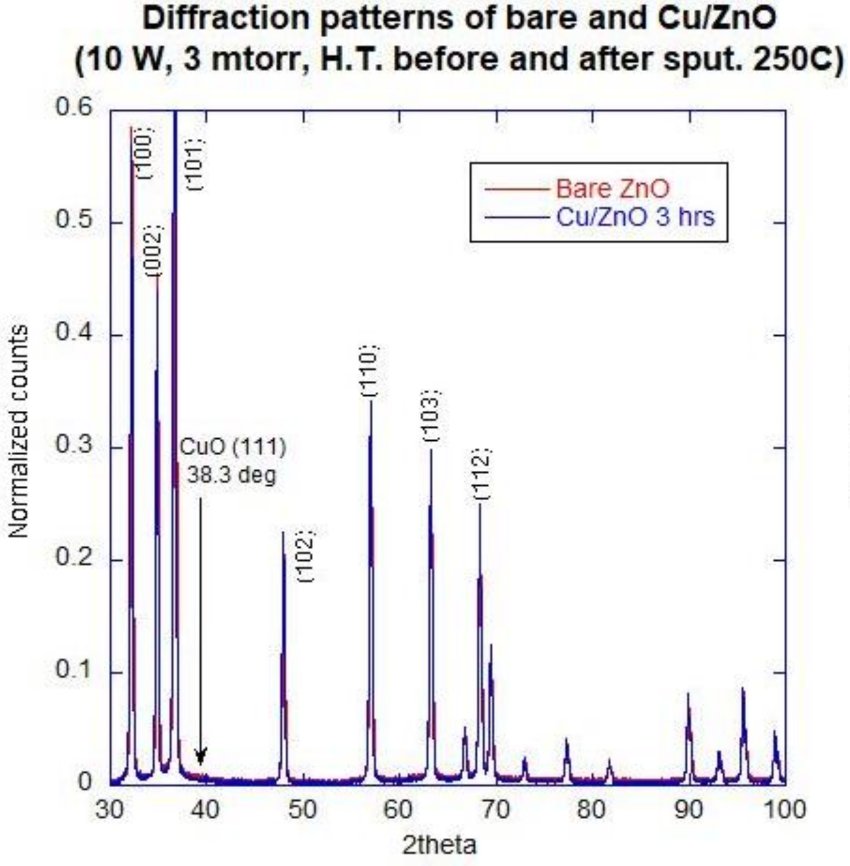
INDIVIDUAL Cu ATOMS

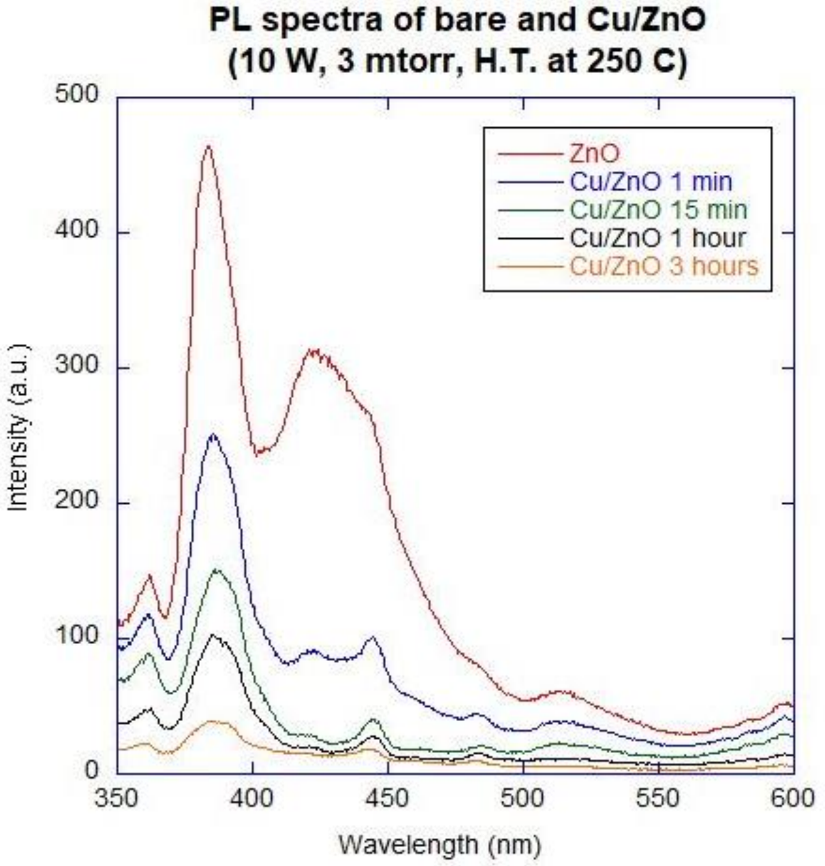


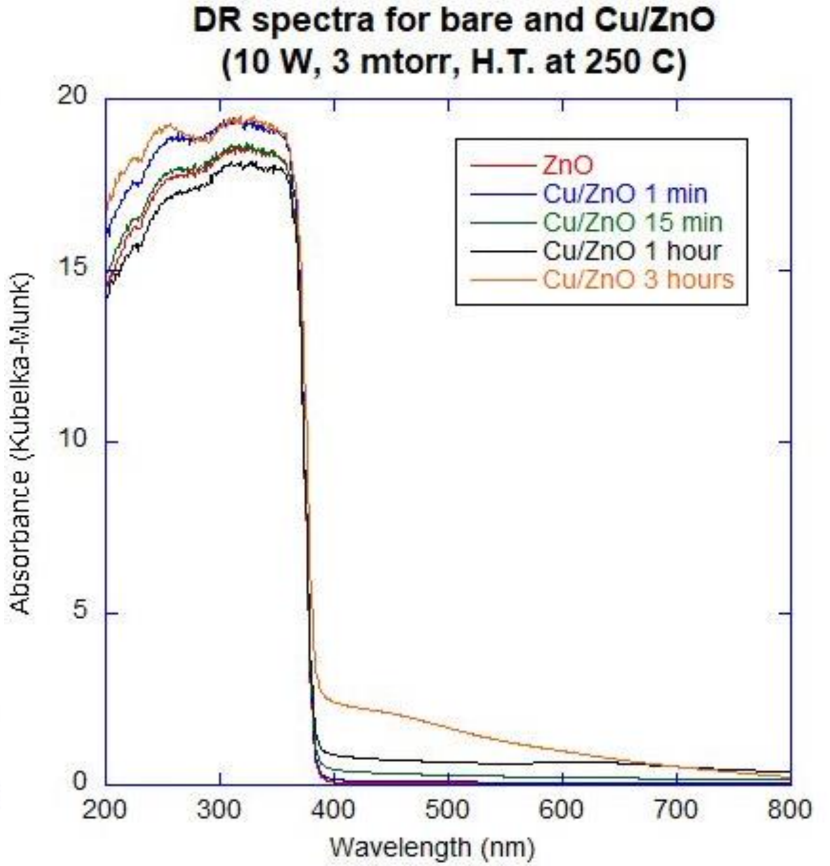
Cu Atoms appear to decorate MgO(100) surface steps

Z-contrast STEM performed in collaboration with G. Duscher (UTK JIAM) and M. Chisholm (ORNL)

What happens if we choose ZnO?

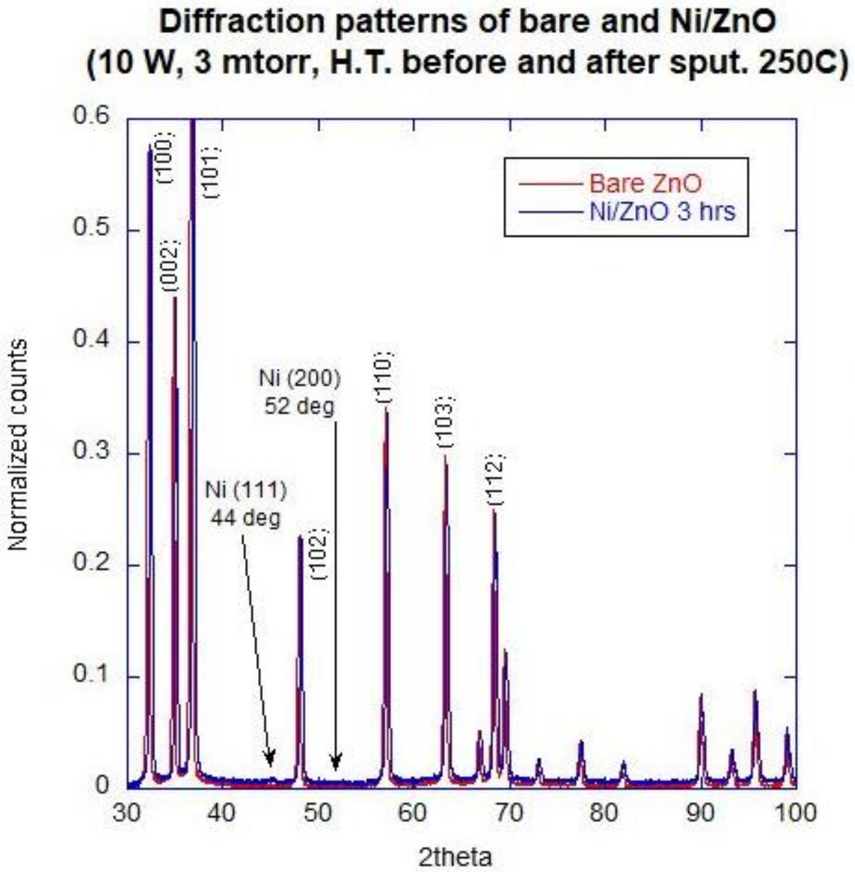




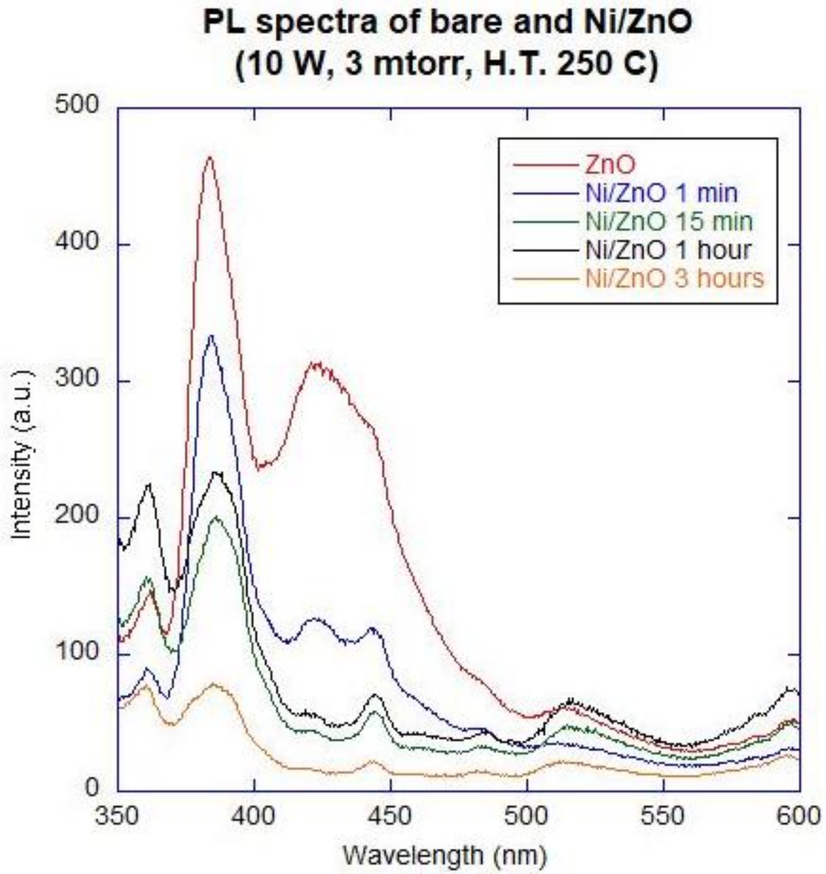


- Crystalline structure (wurtzite) does not show clear additions as when MgO is the substrate
- PL undergoes quenching as with MgO: notice modification of one of the two main bands
- Characteristic strong absorbance in the UV; increasing absorbance in the visible with deposited amount

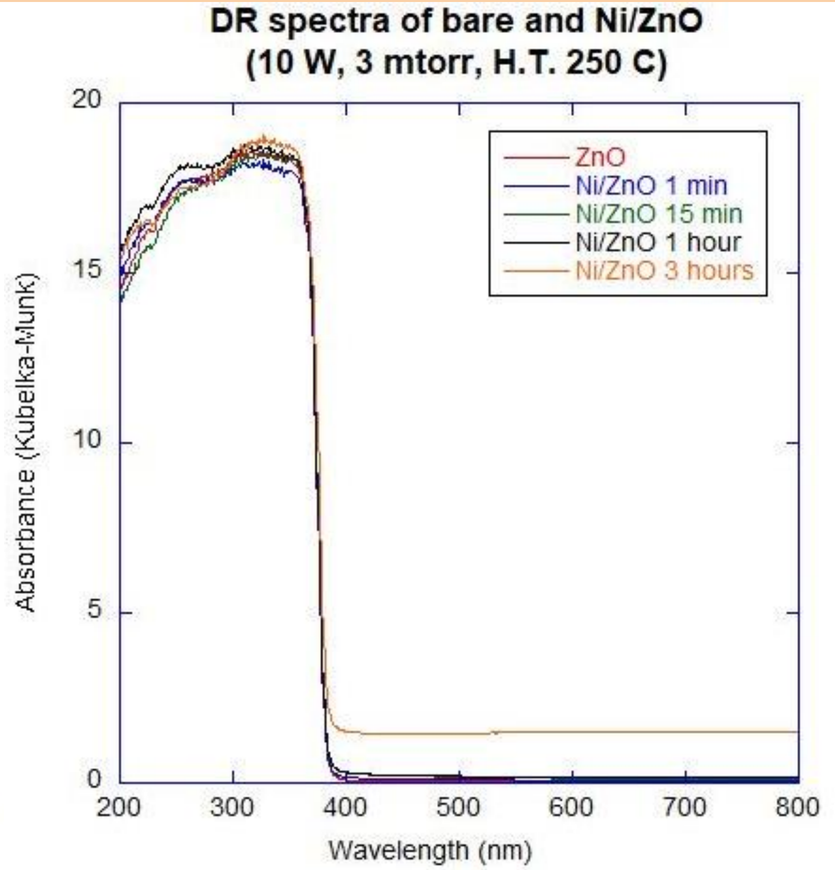
Ni/ZnO



Diffraction patterns of bare and Ni/ZnO
(10 W, 3 mtorr, H.T. before and after sput. 250C)
Bare ZnO
Ni/ZnO 3 hrs
(100)
(002)
(101)
Ni (200)
52 deg
Ni (111)
44 deg
(102)
(110)
(103)
(112)
Normalized counts
2theta

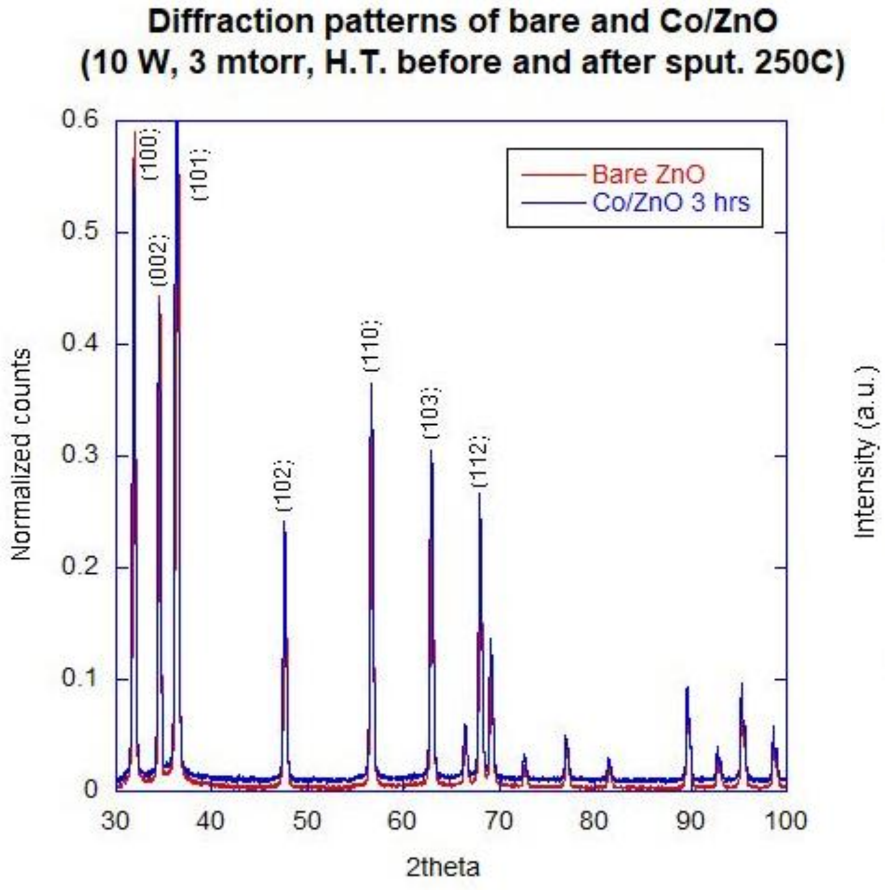


PL spectra of bare and Ni/ZnO
(10 W, 3 mtorr, H.T. 250 C)
ZnO
Ni/ZnO 1 min
Ni/ZnO 15 min
Ni/ZnO 1 hour
Ni/ZnO 3 hours
Intensity (a.u.)
Wavelength (nm)

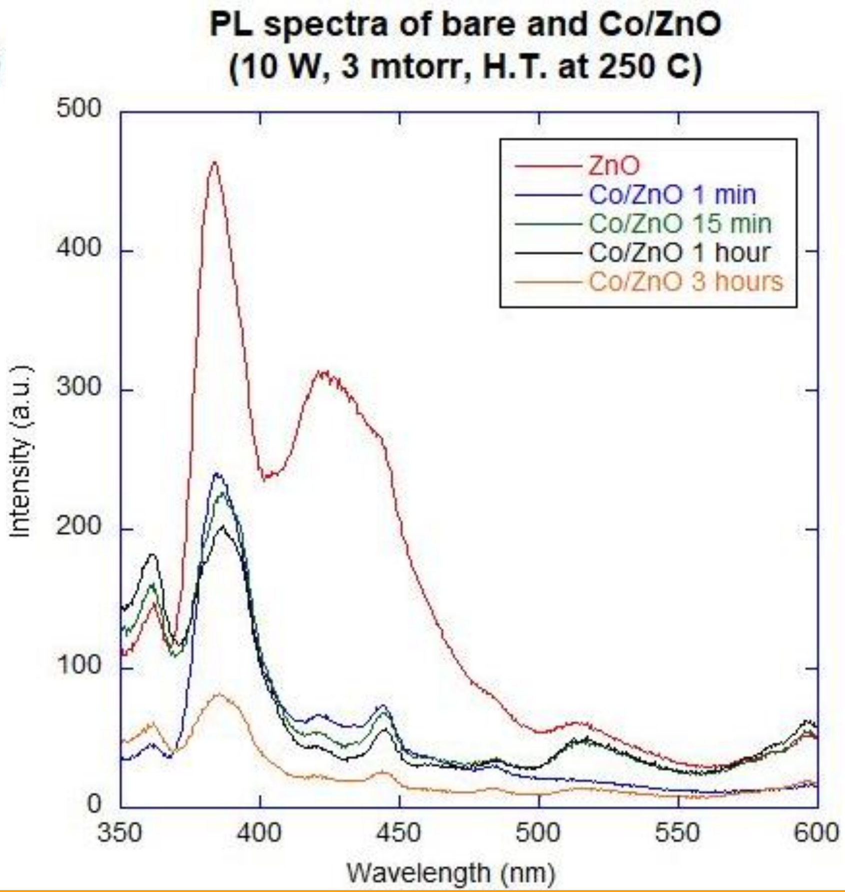


DR spectra of bare and Ni/ZnO
(10 W, 3 mtorr, H.T. 250 C)
ZnO
Ni/ZnO 1 min
Ni/ZnO 15 min
Ni/ZnO 1 hour
Ni/ZnO 3 hours
Absorbance (Kubelka-Munk)
Wavelength (nm)

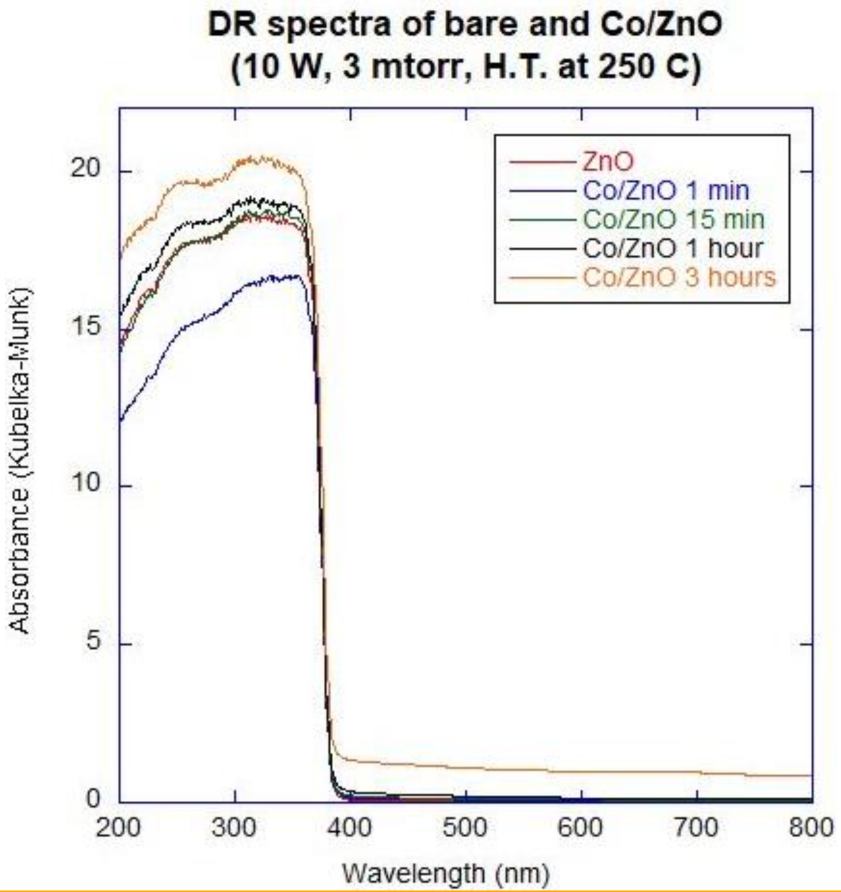
Co/ZnO



Diffraction patterns of bare and Co/ZnO
(10 W, 3 mtorr, H.T. before and after sput. 250C)
Bare ZnO
Co/ZnO 3 hrs
(100)
(002)
(101)
(102)
(110)
(103)
(112)
Normalized counts
2theta
0.6
0.5
0.4
0.3
0.2
0.1
0
30
40
50
60
70
80
90
100



PL spectra of bare and Co/ZnO
(10 W, 3 mtorr, H.T. at 250 C)
ZnO
Co/ZnO 1 min
Co/ZnO 15 min
Co/ZnO 1 hour
Co/ZnO 3 hours
Intensity (a.u.)
Wavelength (nm)
500
400
300
200
100
0
350
400
450
500
550
600



DR spectra of bare and Co/ZnO
(10 W, 3 mtorr, H.T. at 250 C)
ZnO
Co/ZnO 1 min
Co/ZnO 15 min
Co/ZnO 1 hour
Co/ZnO 3 hours
Absorbance (Kubelka-Munk)
Wavelength (nm)
20
15
10
5
0
200
300
400
500
600
700
800

Future perspectives: oxidation states on the surface

- Sputtering-based deposition methodology proves **viable** in order to obtain small metal deposits on MO surfaces.

- Structural and optical measurements indicate the **formation of small metal clusters** (PXRD) and possibly formation of layers, especially on optically active sites/regions.

- Peculiar magnetic character at $T < 50$ K might indicate presence of small **Cu_2O particles** in Cu/MgO and their **magnetic anisotropy** (preferential order of spins).

- Eventually, **electron microscopy confirms previous results**.

- Catalytic and energy-related applications strongly depend on the **oxidation state** of the metal deposits.

- We are performing **X-ray photoemission experiments** to determine metals oxidation states on the substrates; successive step would encompass reaction measurements to **test catalytic activity** of the modified materials.

Overview

- ✓ From macro to micro: the “nanoparticle revolution”
- ✓ Motivation: importance of nanomaterials in energy applications
- ✓ Metal decoration of metal oxides
  - Choice of materials
  - Experimental apparatus and methodology
- ✓ Characterization of decorated materials: evidence of metal deposits
- ✓ Future prospects of our work
- ✓ Deposition methods for cavities applications @Fermilab

Materials play a fundamental role

Importance of materials to maximize Q-factor in SRF cavities

- Improve field gradients in cavities cells
- Reduce construction costs
- Limit materials degradation

COUPLING OF RF POWER TO CAVITY CELLS

FIND THE RIGHT RECIPES TO ENHANCE SUPERCONDUCTING PERFORMANCES w/COST-EFFECTIVE SOLUTIONS

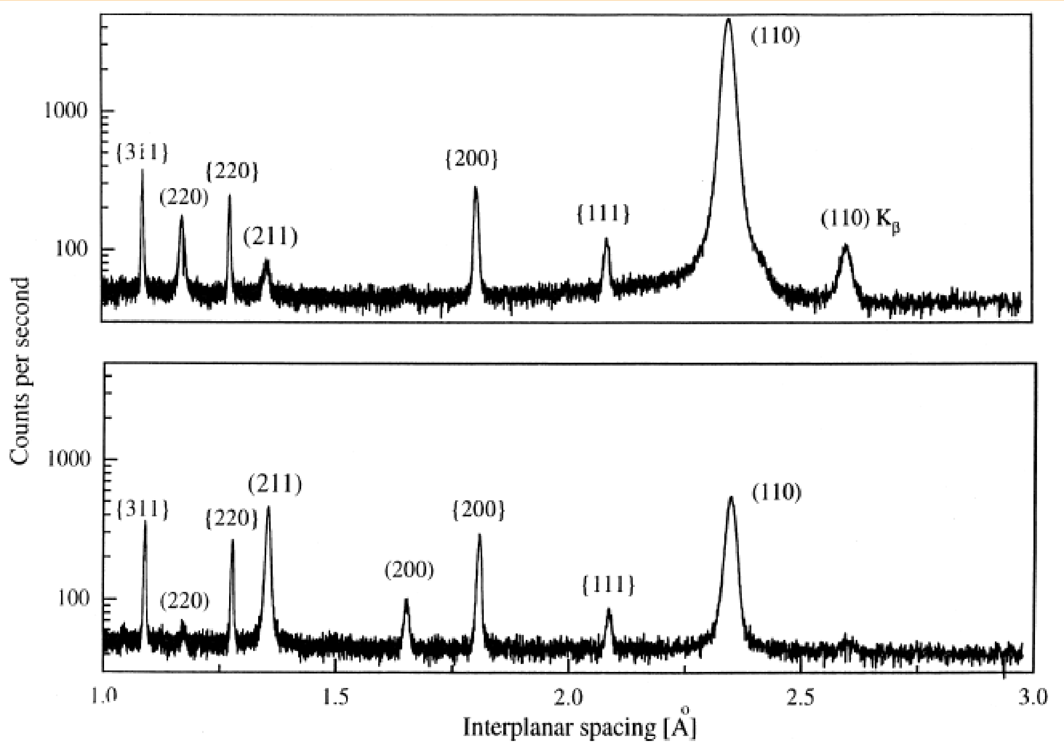
ROBUSTNESS AND QUALITY OF MATERIALS: VERY INTENSE FIELDS AND LOW TEMPERATURES

SCALABILITY FOR DIFFERENT APPLICATIONS

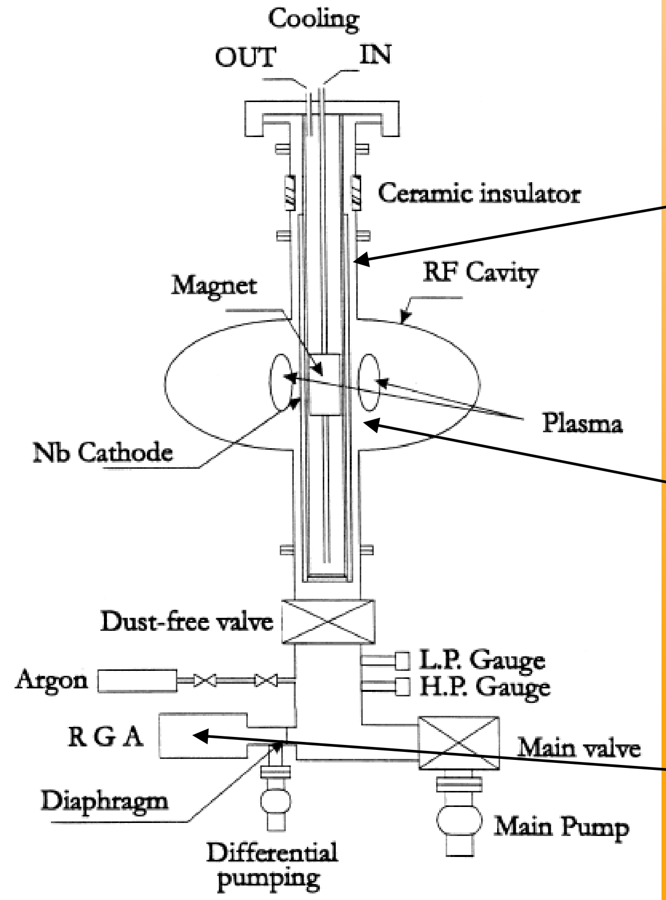
Characterizing new materials solutions

Nb-coated bulk Cu cavities by means of magnetron sputtering

Surface resistance of superconducting Nb films (1.5 GHz): **XRD** to study purity of layers



Benvenuti et al., *Physica C* 316 (1999) 153-188.



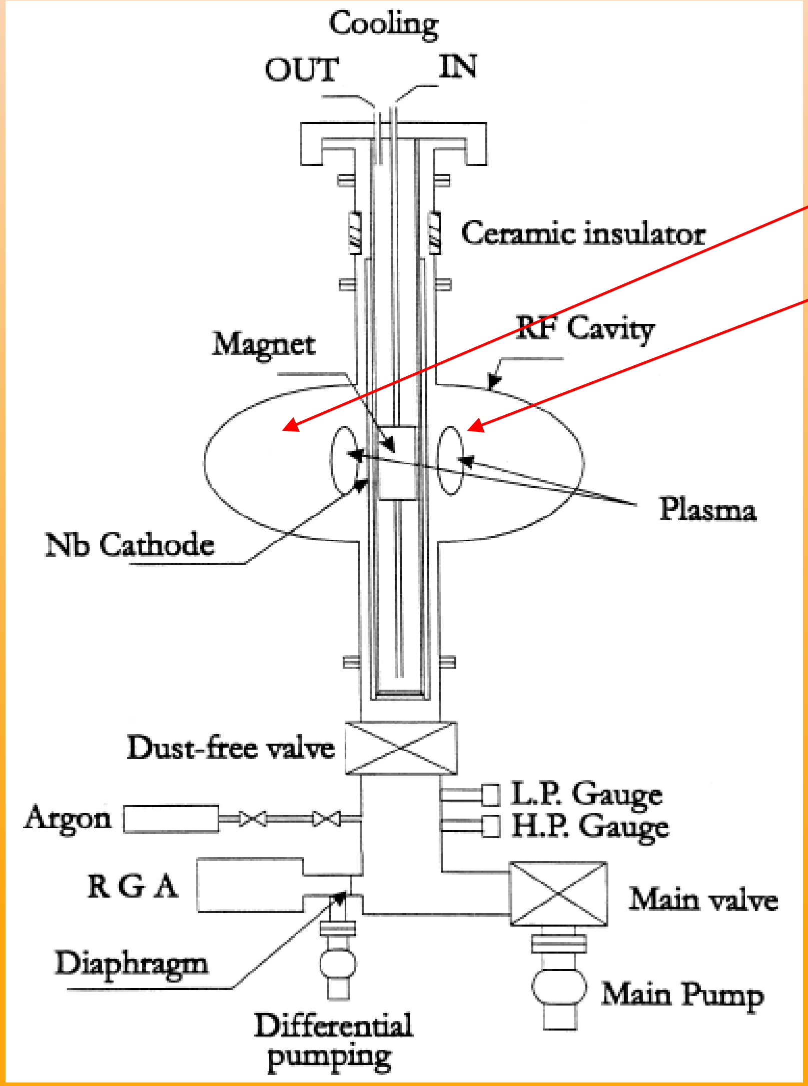
Cylindrical Nb cathode to sputter onto inner walls of cavity

Flux dependence on angle and distance

RGA (to monitor impurities)

Measuring sputtering flux inside cavities

Idea: design cavity vacuum environment to host a custom-made QCM assembly to monitor metal deposition



Benvenuti et al., *Physica C* 316 (1999) 153-188.

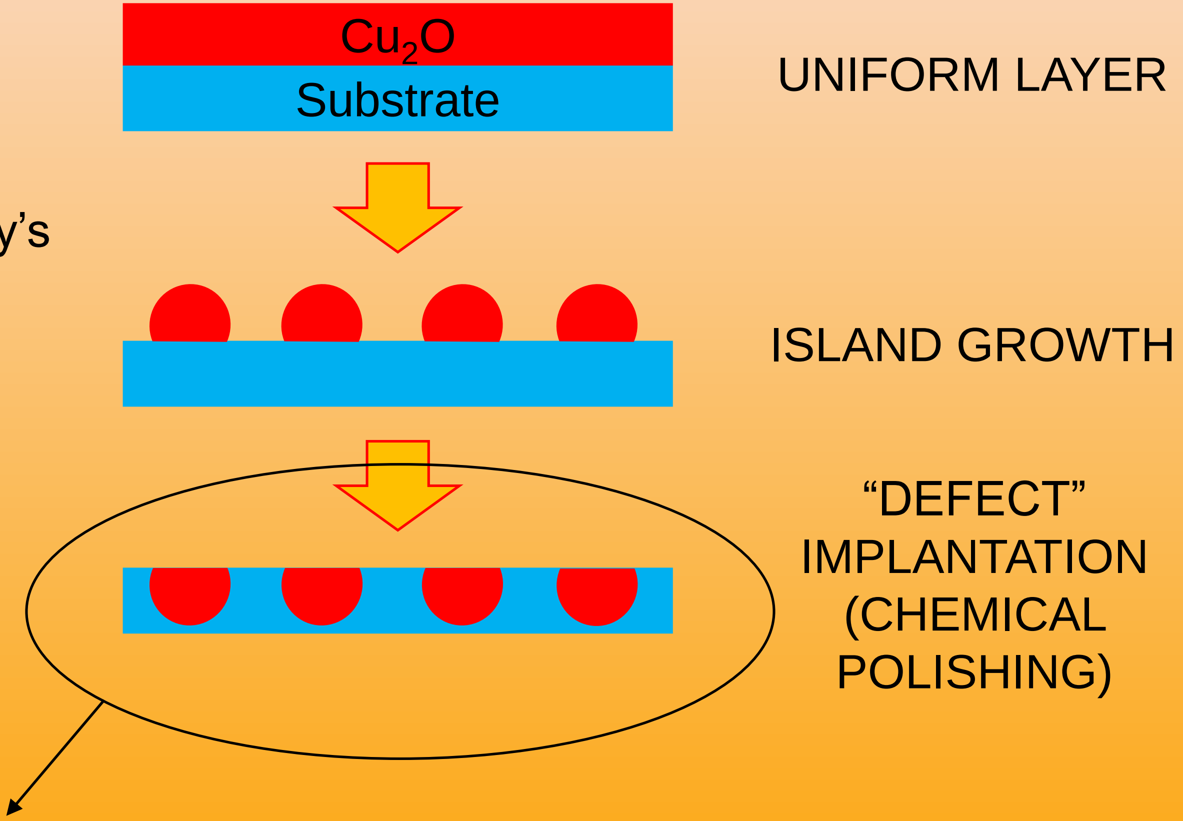
QCM inserts

QCM sensor can be designed to rotate 360° all around inside cavity in order to precisely measure angle and distance dependence of sputtering flux

Produce high-quality homogeneous films of a superconducting material of interest

What about reactive sputtering?

- Copper-oxide materials appear as a new class of promising high-T_C superconductors
- What about trying to **embed** them into cavity's inner surface?
- In fact, a **higher T_C superconductor** would improve cavity's **Q-factor** while **reducing refrigeration energy**

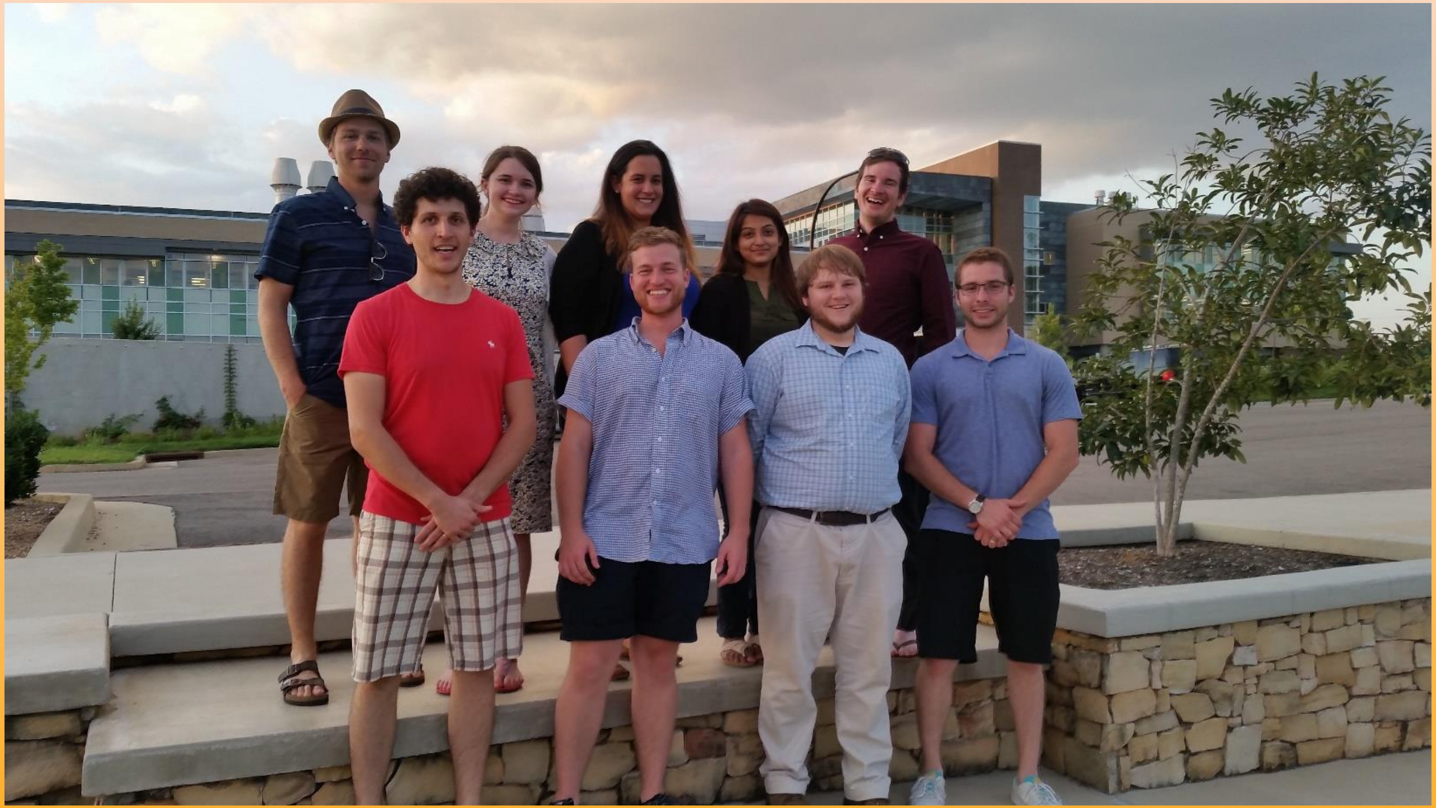


Imagine other combinations of inert and reactive sputtering gases, i.e. Kr or Xe instead of Ar (inert gas) and N_2 instead of O_2 (to induce a reaction): this might lead to new, efficient and also scalable solutions for cavities technology, e.g. new **doping** solutions.

Conclusions

- Metal oxide materials can be produced with high quality in powdered form.
- The interest in their properties as supports for metal nanoparticles is driven by heterogeneous catalysis, as well as a potential for novel energy applications.
- A new magnetron sputtering-based methodology is a viable solution to achieve decoration of metal oxide materials (as shown by materials characterization).
- Final goal is to learn the electronic structure and activity of the novel materials.
- Learning materials properties at the nanoscale can open new avenues toward solving more macroscopic problems (e.g. SRF cavities) utilizing herein presented experimental methods (sputtering, QCM, XRD, …).

Acknowledgements



Larese group at JIAM

http://materials.chem.utk.edu/index_larese_group.html

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Chemistry Department

Thank you!