DRAFT:
Metal Oxide based Nanostructure for Multifunctional Devices Applications.

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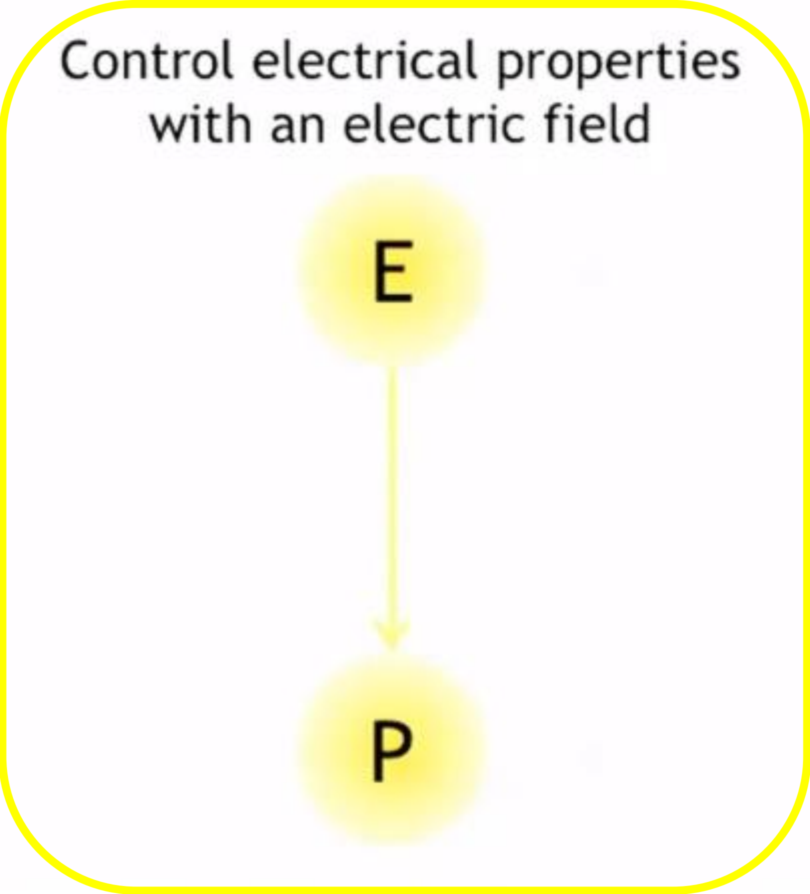
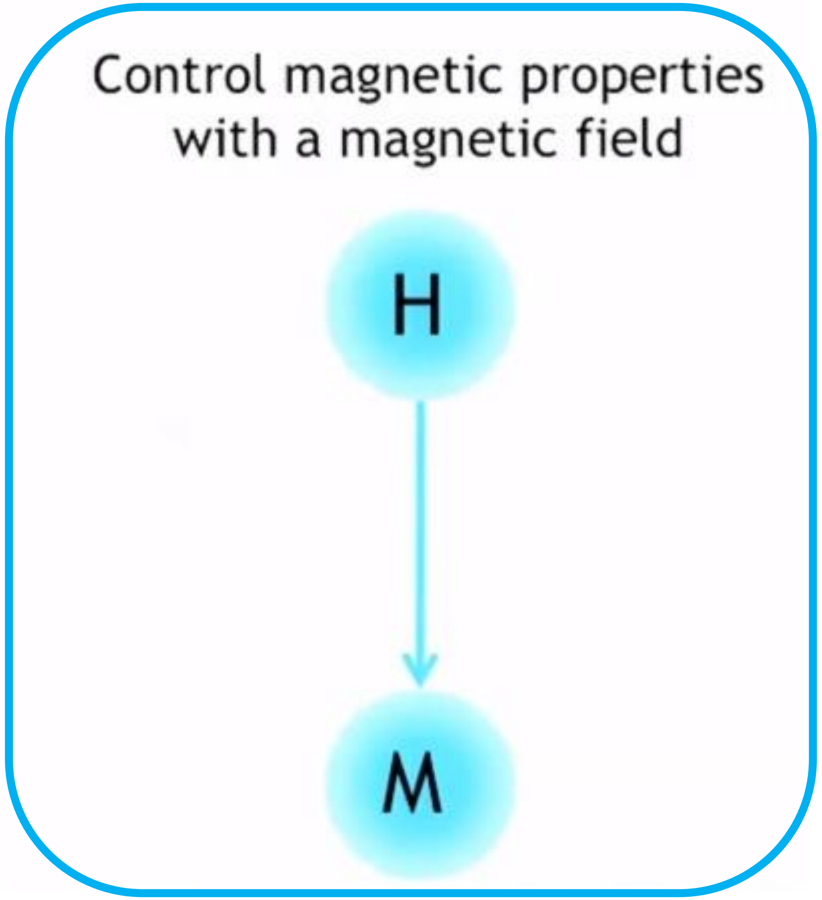
Functionality: Magnetoelectric Response

Controlling P and M with E and H fields

Usually:



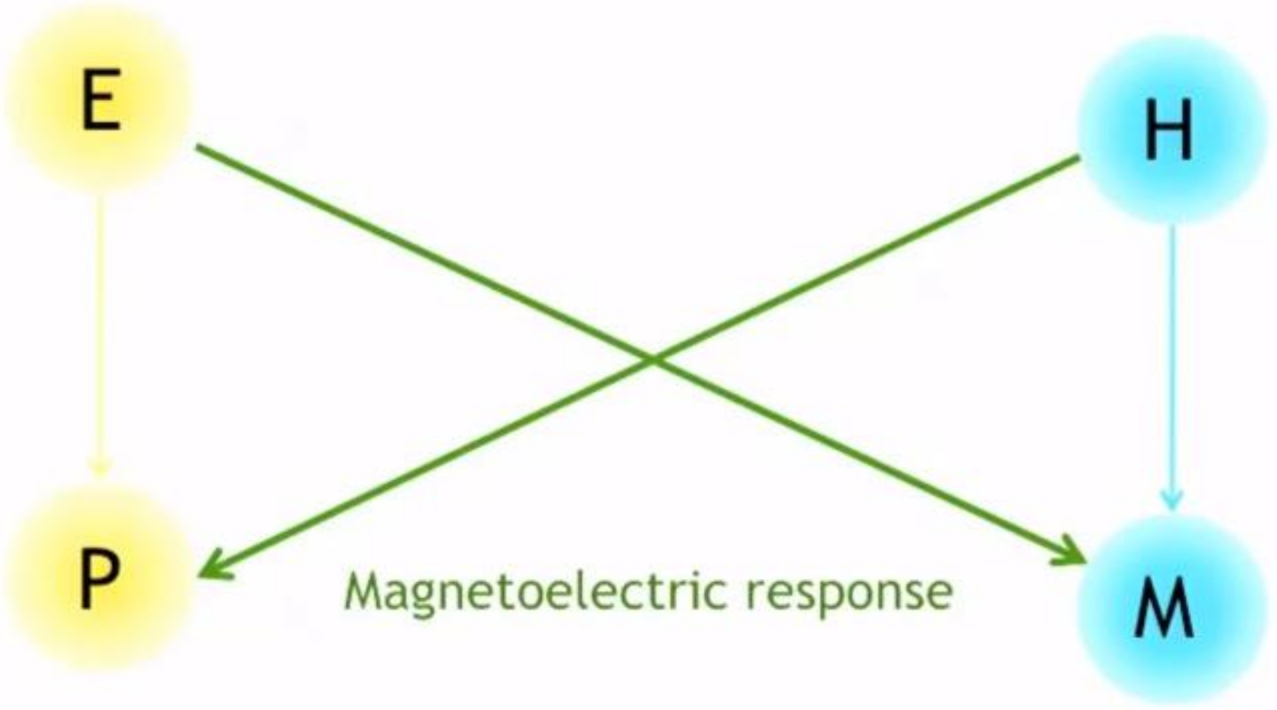
Control electrical properties with an electric field



Control magnetic properties with a magnetic field

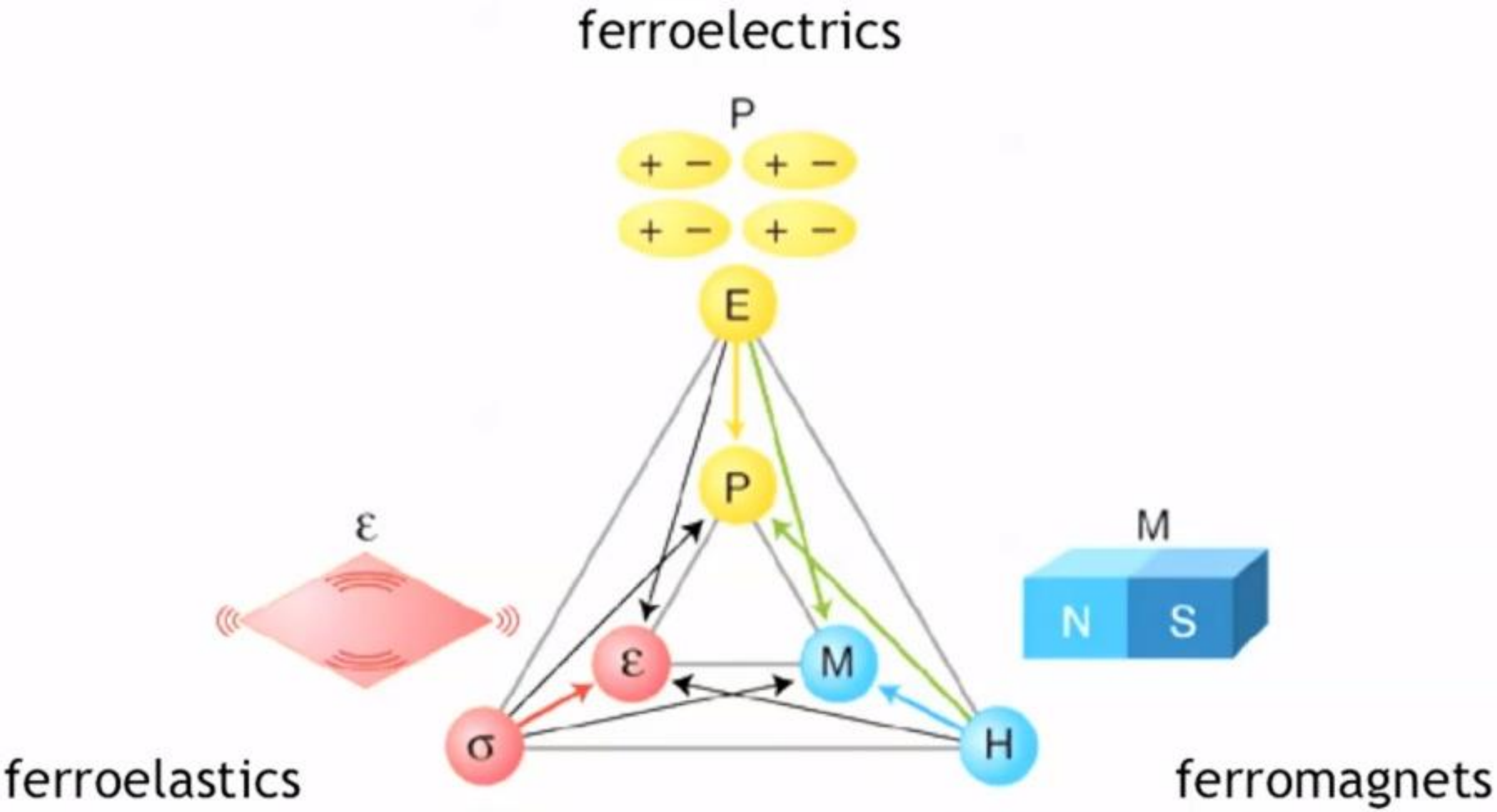
Functionality: Magnetoelectric Response

Instead:



Magnetoelectric response

Multiferroics and Magnetoelectricity

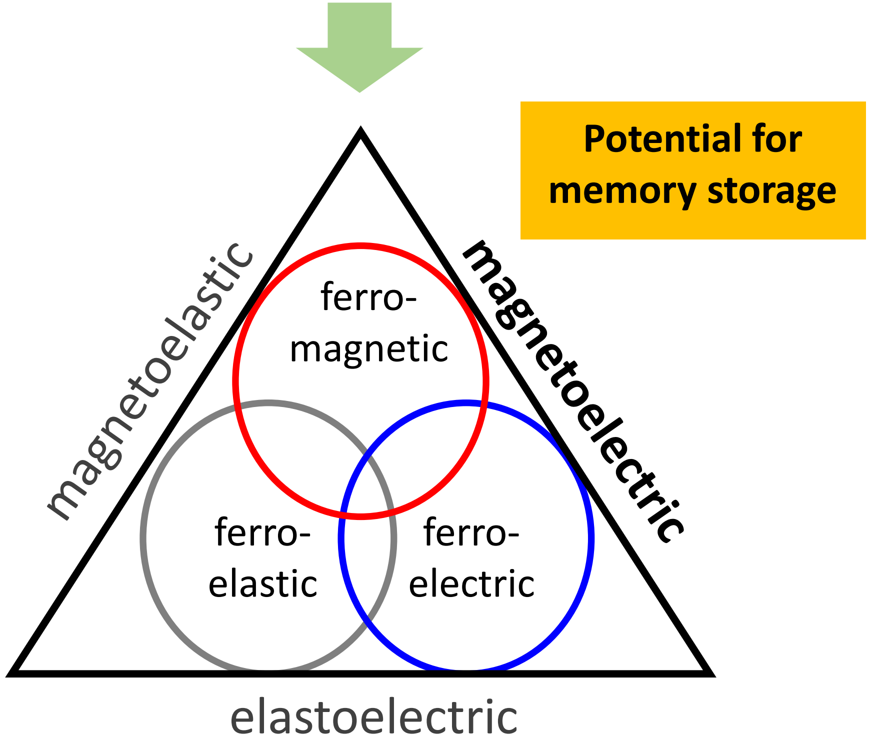


The renaissance of magnetoelectric multiferroics,
N. A. Spaldin and M. Fiebig, Science **15**, 5733 (2005)

Multiferroic: Potential of multifunctionality

Multiferroic (materials) characteristic → multifunctional devices

→Simultaneous existence of two or more ferroic orders in one material system.

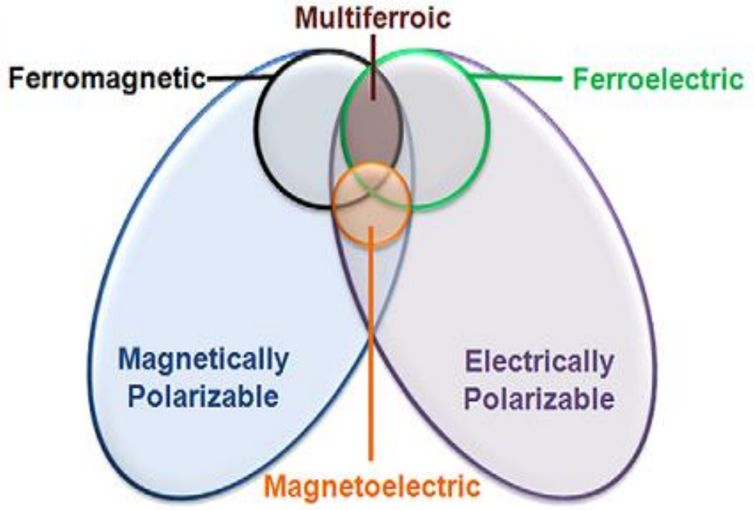


Potential for memory storage

Relation between ferroelectric and ferromagnetic in multiferroic system

Ferroelectric **(FE):** electrically polarizable >< **Ferromagnetic (FM):** magnetically polarizable

→ Coexistence FE and FM in the systems generates multiferroic characteristic (magnetoelectric).



(Eerenstein *et al.*, *Nature*, 2006, **442**, 759

However,….

Challenge → to simultaneously produce ferroelectric and ferromagnetic

▪**Ferroelectric**

•appears in material with high crystallinity (low defects).

•possess ions that have a formal $3d^0$ electronic state.

▪**Ferromagnetic**

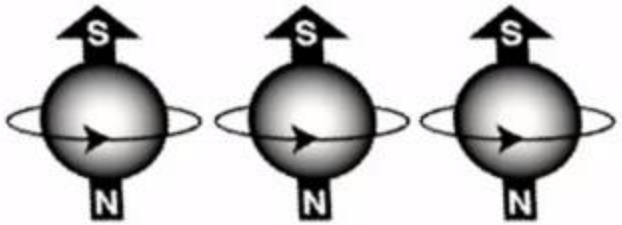
•appears in material with low crystallinity (high defect).

•possess incompletely filled 3d shells.

Why are there so few magnetic ferroelectrics?

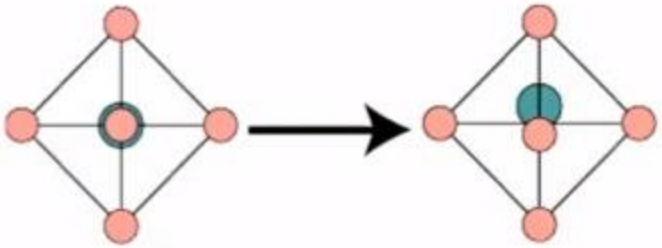
the chemistry that promotes one functionality often prohibits another

Ferromagnetism



Requires partially filled *d* orbitals
(Hund versus Pauli)

Ferroelectricity



Requires empty *d* orbitals; “Matthias rule”
(covalency versus Coulomb repulsion)

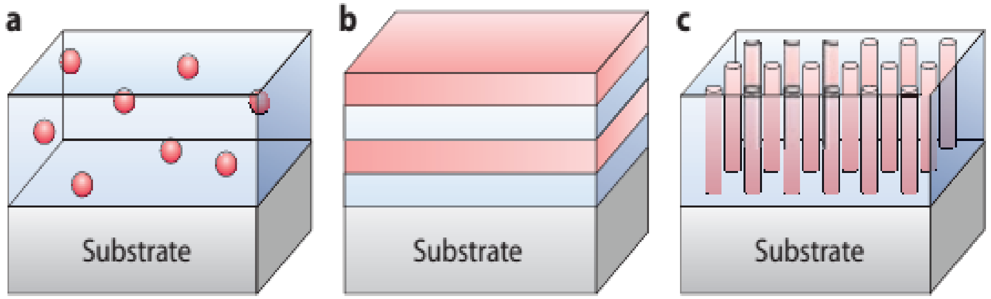
CHEMICALLY CONTRA-INDICATED!

B.T. Matthias, *New ferroelectric crystals*, Phys. Rev. (1949)
N.A. Hill, *Why are there so few magnetic ferroelectrics?* J. Phys. Chem. B 104, 6694 (2000)

Solution?

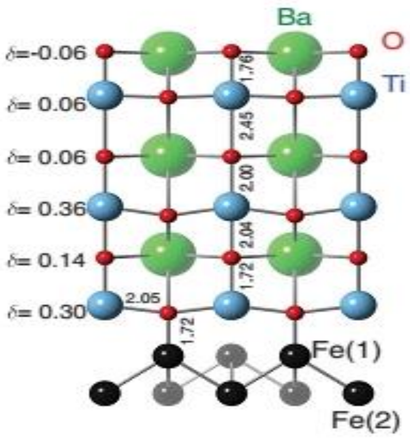
Ferroelectric and ferromagnetic materials is combined in several configuration.

(1) Composite



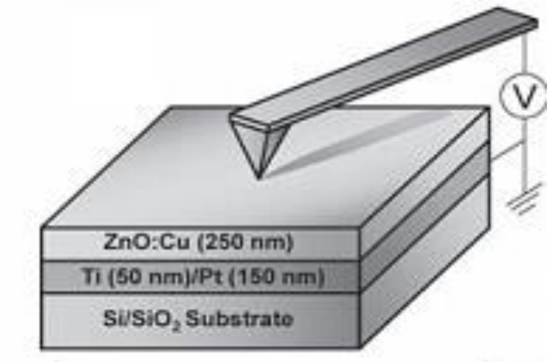
Y. Wang, *et al. NPG Asia Mater.*, 2010, **2**(2) 61–68

(2) Interface effects



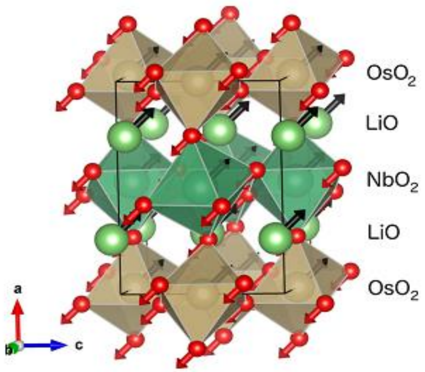
Meyerheim *et al.*, *Phys. Rev. Lett.*, 2011, **106**, 0872032011

(3) Doping



T. S. Herng *et al.*, *Adv. Mater.*, 2011, **23**(14), 1635-1640

(4) Superlattice



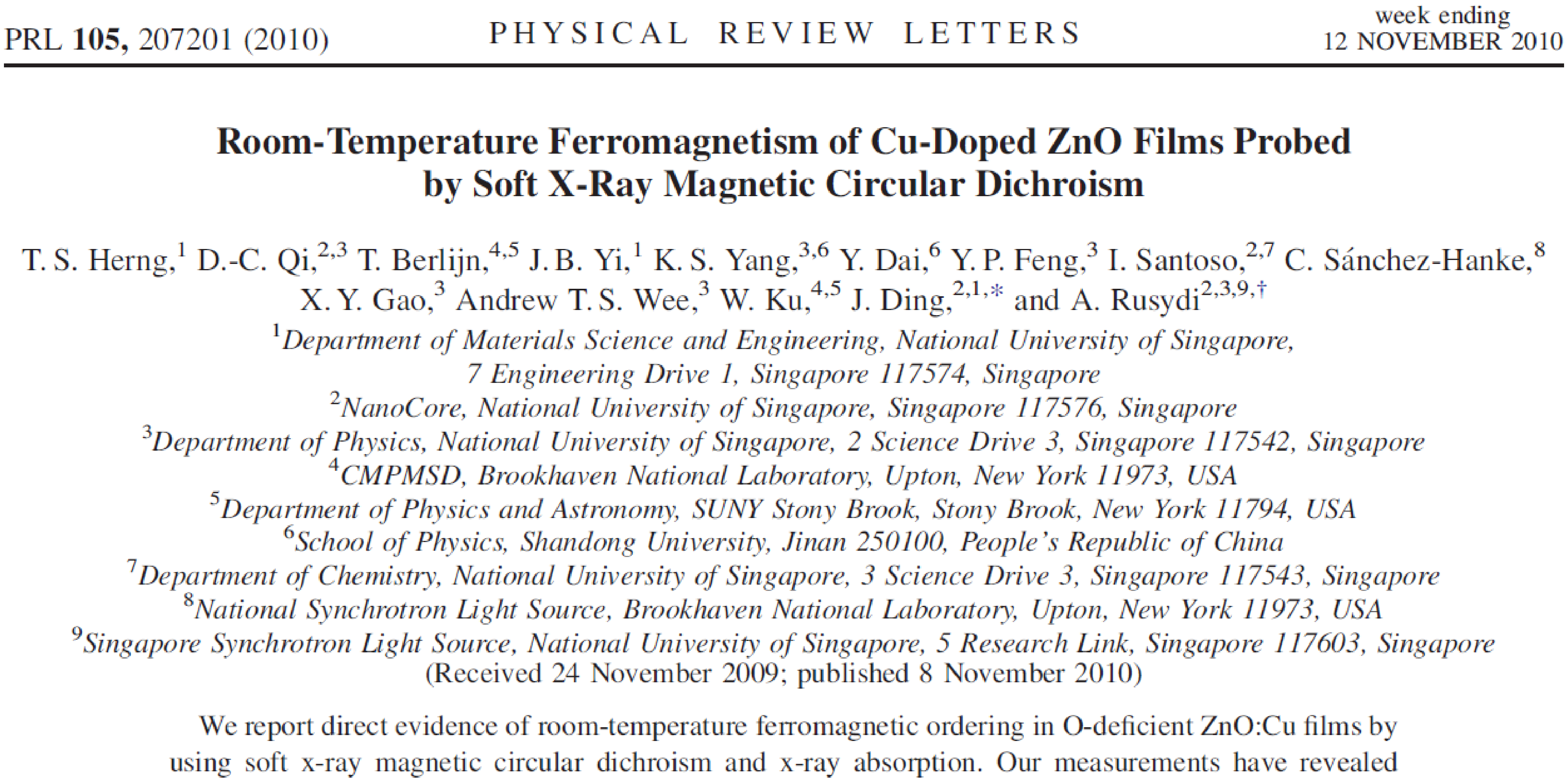
Puggioni *et al.*, *Phys. Rev. Lett.*, 2015, **115**, 087202

ZnO

Electronics,

Optic and

Magnetic



PRL **105,** 207201 (2010) PHYSICAL REVIEW LETTERS week ending 12 NOVEMBER 2010

Room-Temperature Ferromagnetism of Cu-Doped ZnO Films Probed by Soft X-Ray Magnetic Circular Dichroism

T. S. Herng,[1] D.-C. Qi,[2,3] T. Berlijn,[4,5] J. B. Yi,[1] K. S. Yang,[3,6] Y. Dai,[6] Y. P. Feng,[3] I. Santoso,[2,7] C. Sánchez-Hanke,[8] X. Y. Gao,[3] Andrew T. S. Wee,[3] W. Ku,[4,5] J. Ding,[2,1,*] and A. Rusydi[2,3,9,†]
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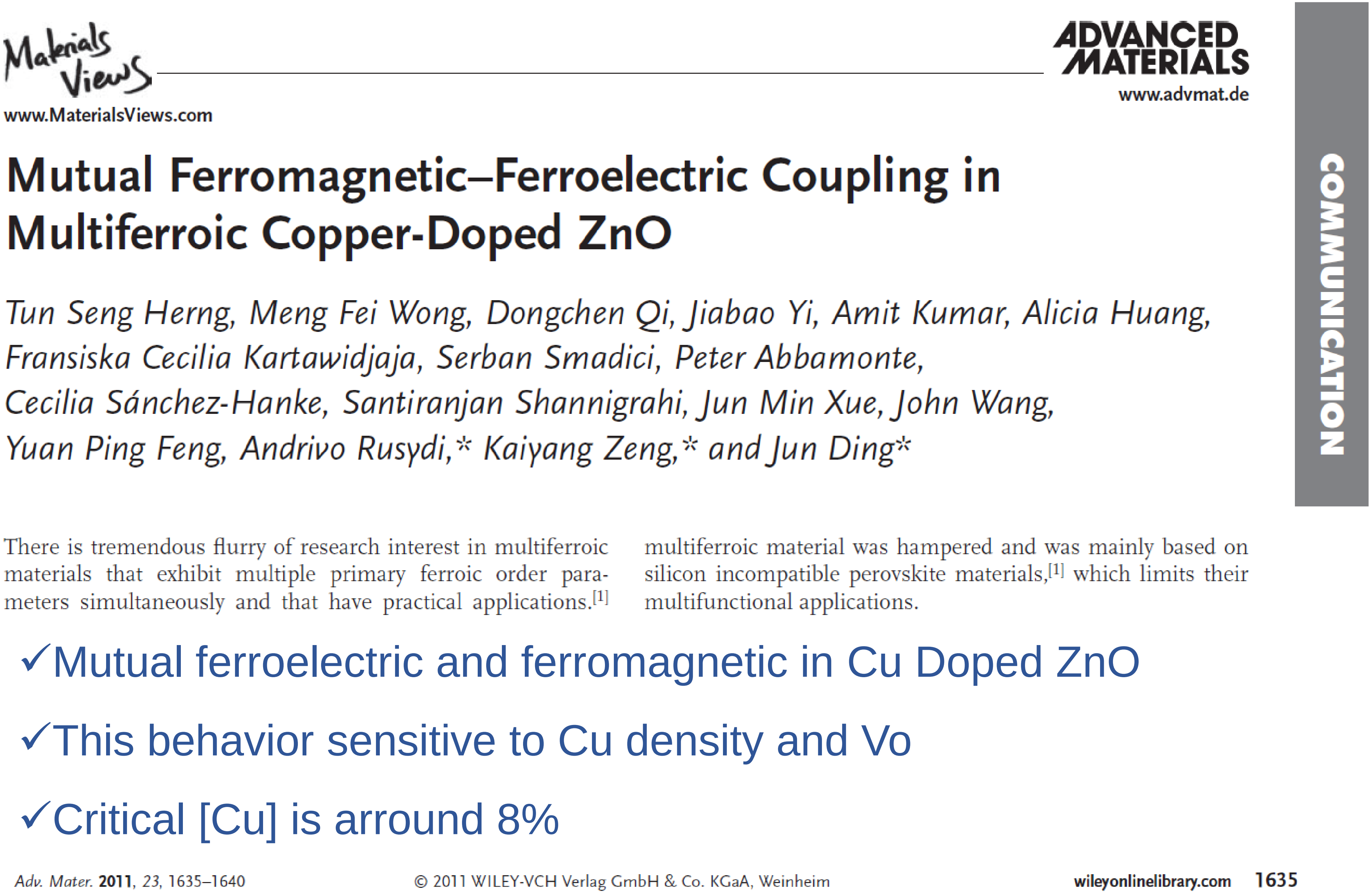
(Received 24 November 2009; published 8 November 2010)

We report direct evidence of room-temperature ferromagnetic ordering in O-deficient ZnO:Cu films by using soft x-ray magnetic circular dichroism and x-ray absorption. Our measurements have revealed

- ✓RT Ferromagnetism (FM) of 2% Cu doped ZnO
- ✓Vo contribution and Cu impurities is essential to observe FM
- ✓Large size vacancies orbital→ by first principle calculation.



Materials Views
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

COMMUNICATION

Mutual Ferromagnetic–Ferroelectric Coupling in Multiferroic Copper-Doped ZnO

Tun Seng Herng, Meng Fei Wong, Dongchen Qi, Jiabao Yi, Amit Kumar, Alicia Huang, Fransiska Cecilia Kartawidjaja, Serban Smadici, Peter Abbamonte, Cecilia Sánchez-Hanke, Santiranjan Shannigrahi, Jun Min Xue, John Wang, Yuan Ping Feng, Andrivo Rusydi, Kaiyang Zeng,* and Jun Ding**

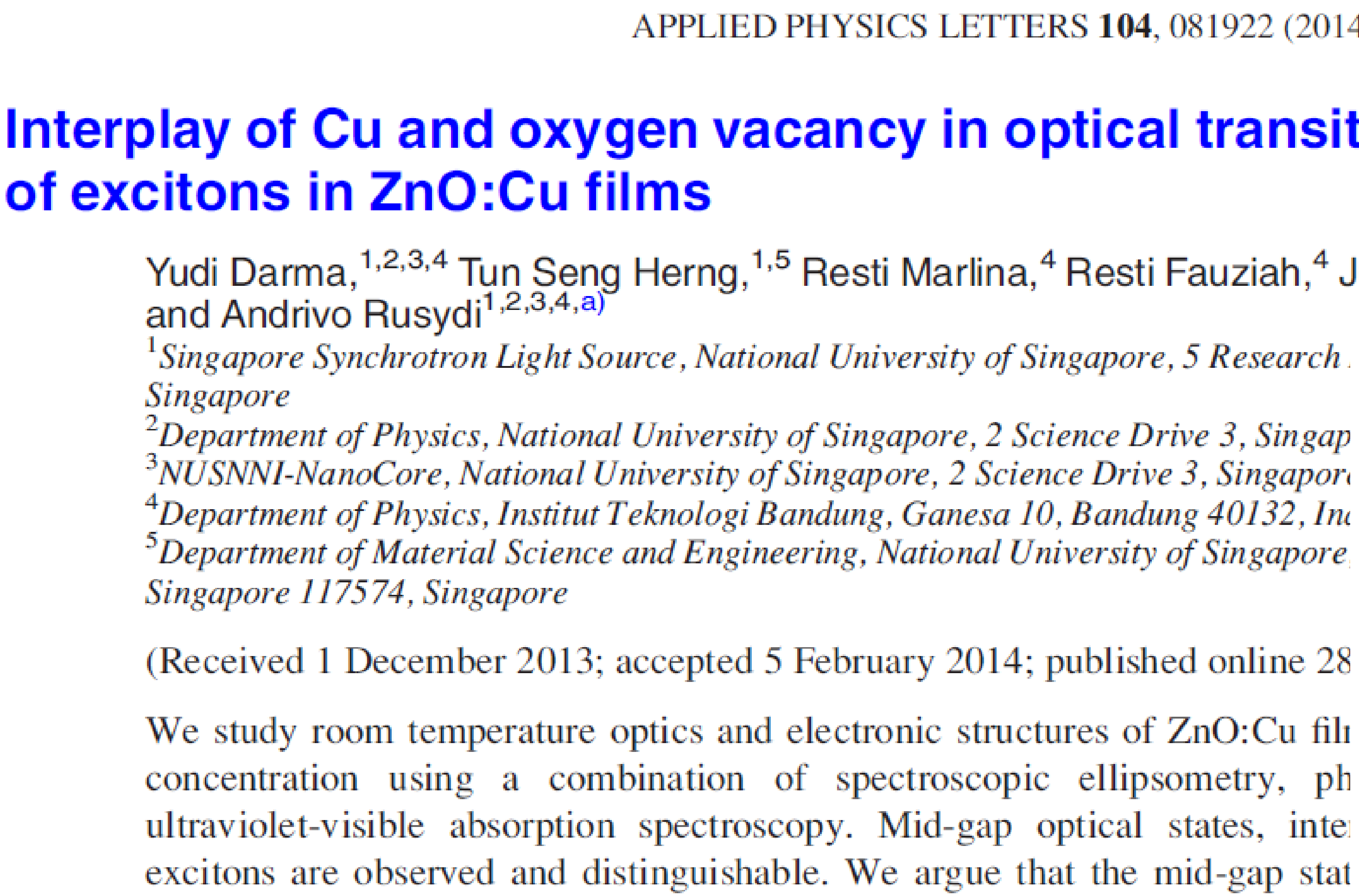
There is tremendous flurry of research interest in multiferroic materials that exhibit multiple primary ferroic order parameters simultaneously and that have practical applications.[1] multiferroic material was hampered and was mainly based on silicon incompatible perovskite materials,[1] which limits their multifunctional applications.

✓Mutual ferroelectric and ferromagnetic in Cu Doped ZnO

✓This behavior sensitive to Cu density and Vo

✓Critical [Cu] is arround 8%

Adv. Mater. **2011**, *23*, 1635–1640



APPLIED PHYSICS LETTERS **104**, 081922 (2014)

Interplay of Cu and oxygen vacancy in optical transitions and screening of excitons in ZnO:Cu films

Yudi Darma,[1,2,3,4] Tun Seng Herng,[1,5] Resti Marlina,[4] Resti Fauziah,[4] Jun Ding,[5] and Andrivo Rusydi[1,2,3,4,a)]

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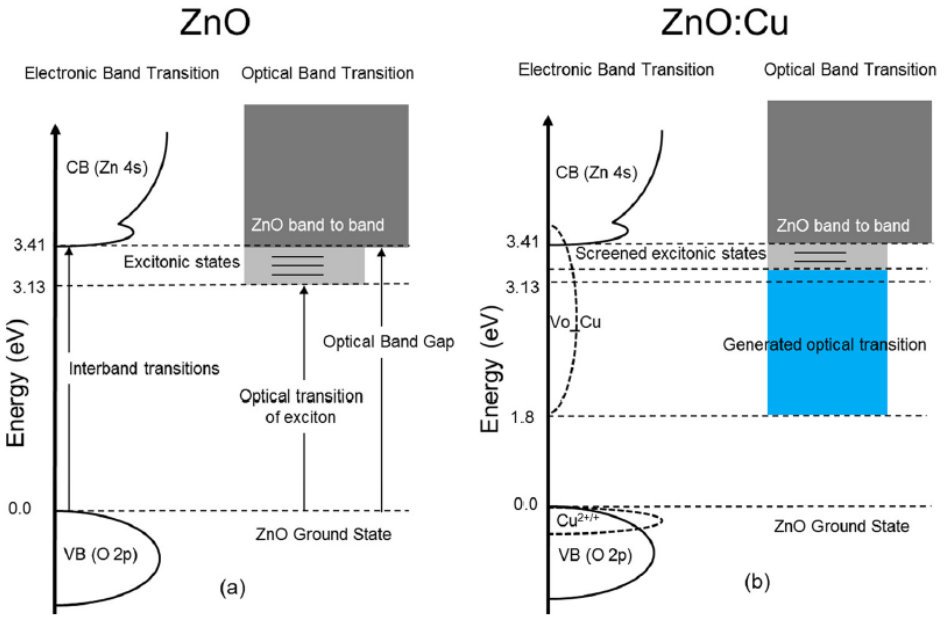
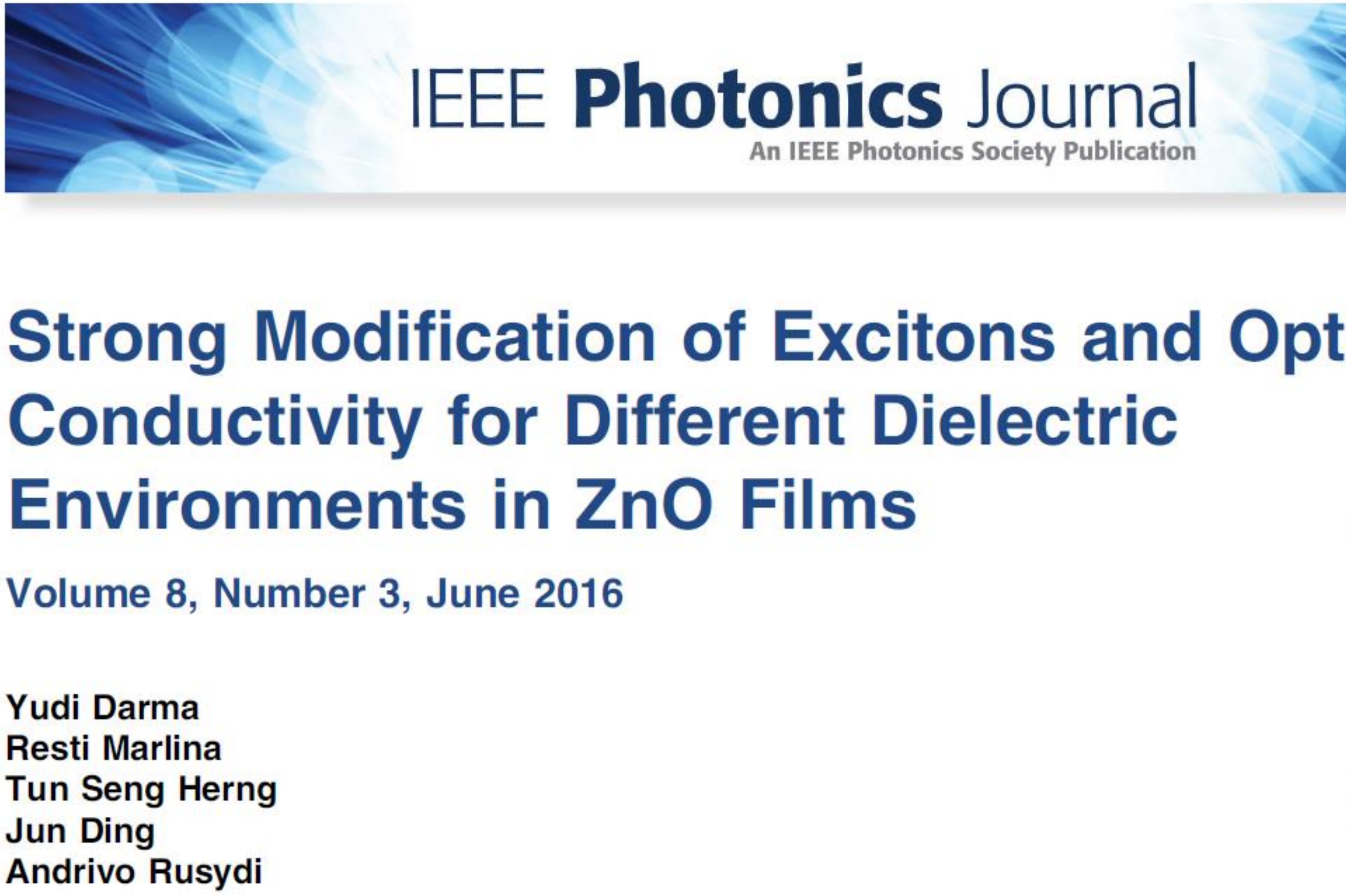
(Received 1 December 2013; accepted 5 February 2014; published online 28

We study room temperature optics and electronic structures of ZnO:Cu fil concentration using a combination of spectroscopic ellipsometry, ph ultraviolet-visible absorption spectroscopy. Mid-gap optical states, inte excitons are observed and distinguishable. We argue that the mid-gap stat



- ✓Observation of exciton and new transition state
- ✓Screening of exciton by transition states
- ✓The role of Cu concentration to optical conductivity



IEEE Photonics Journal
An IEEE Photonics Society Publication

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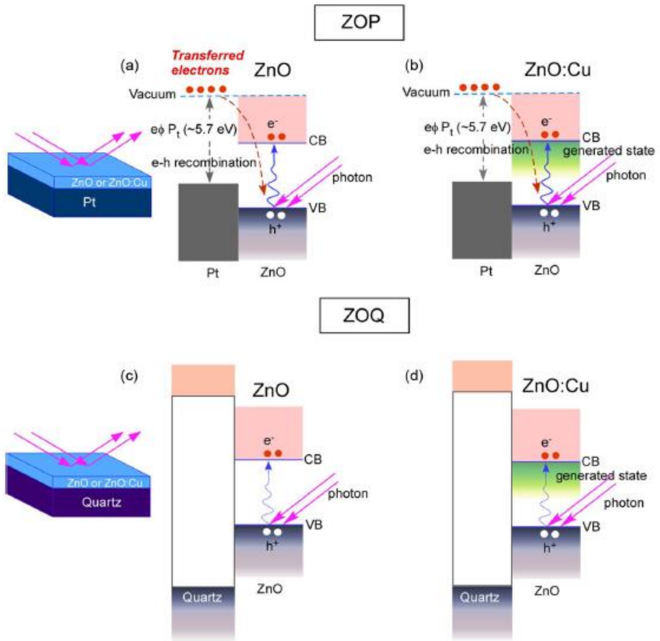
Strong Modification of Excitons and Optical Conductivity for Different Dielectric Environments in ZnO Films

Volume 8, Number 3, June 2016

Yudi Darma
Resti Marlina
Tun Seng Herng
Jun Ding
Andrivo Rusydi



- Electronic blocking and screening effects in ZnO film through dielectric function and optical conductivity as a function of substrates and Cu concentration have been studied systematically
- Strong modification of excitonic states in ZnO films by selecting different electronic environments

Surface modification on ZnO based thin film

→Multiple-stacked nano porous ZnO

Surface modification effect to optical properties

→ Emission enhancement in ZnO are still become the main interest in thin film for photonic/optoelectronics devices

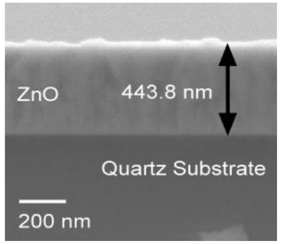
→ZnO Nanocolumnar (NC)

modification of magnetic and electronic properties

→Reduction of ZnO dimension to increase Zn vacancy at the surface

ZnO Film → Multiple-stacked nano porous ZnO

Surface modification effect to optical properties



ZnO Green Emission Sample

PLD

Laser energy ~180mJ, frequency 5Hz

Sample 1

as prepare
Vacuum 10^{-7} mbarr
(no oxygen supply)
RT
~440nm

ZnO
Quartz

Sample 3

ZnO
Quartz

as prepare
$2x\ 10^{-4}$mbarr
(oxygen supply)
600 C
~720nm

H Annealing

annealed in hydrogen(Ar 95%+H5%)
570 C for 1hour.

The films were placed in the tube furnace at the room temperature and the temperature rate of heating and cooling was set 5C/min.

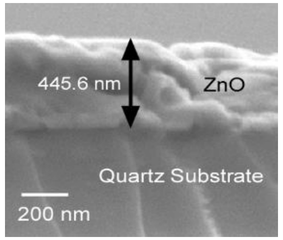
Sample 2

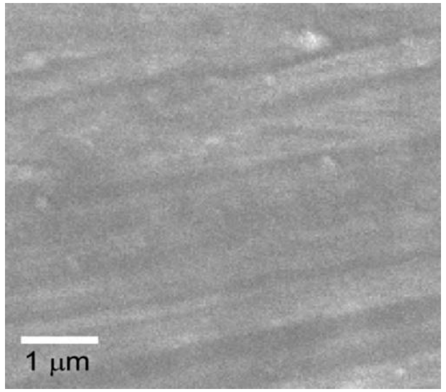
ZnO
Quartz

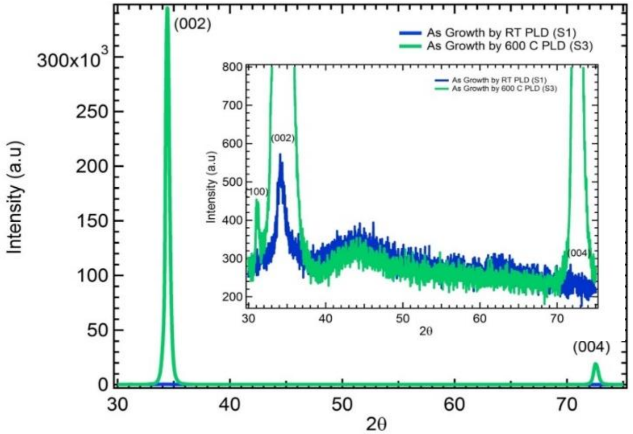
Sample 4

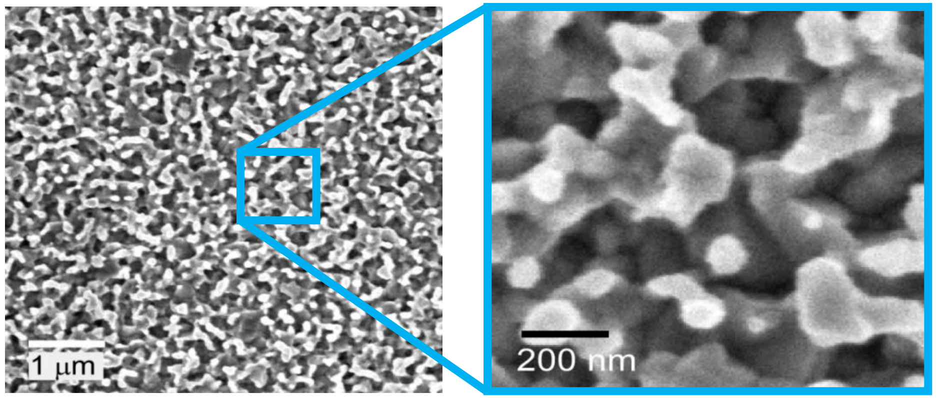
ZnO
Quartz

H2 Anneal
570 C , 1 Hour
~760nm





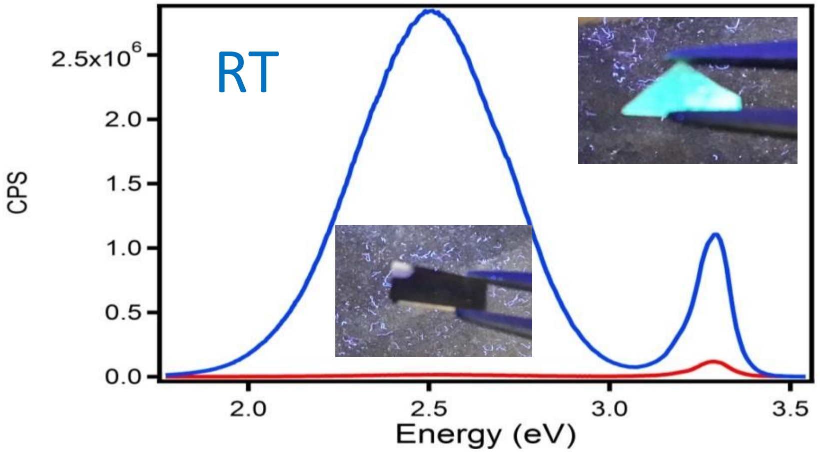


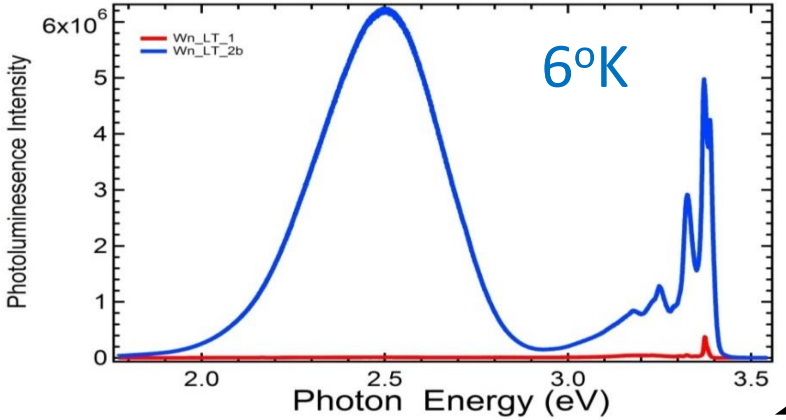


App Surf Sci. (2018) 462, 466-470

Phys Stat Solidi A (2018) 1800458

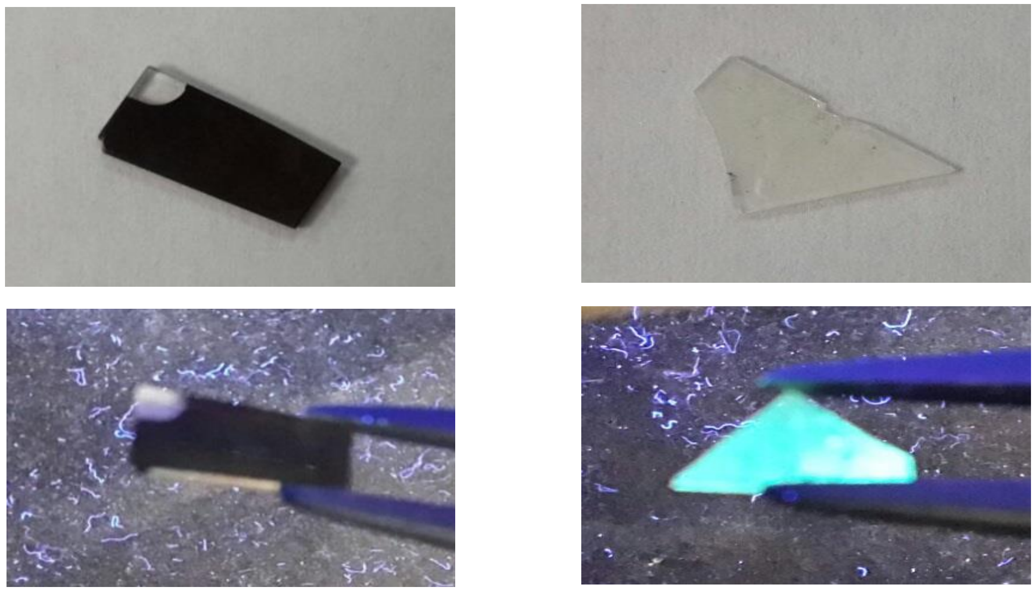
Photoluminescence (RT and 6K)

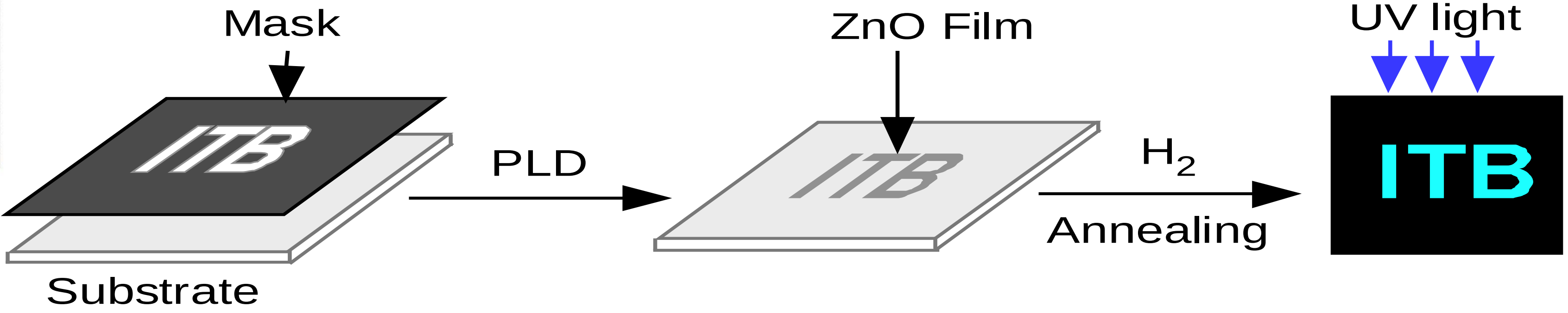




Phys Stat Solidi A (2018) 1800458

UV exposure





App Surf Sci. (2018) **462**, 466-470

ZnO Film → ZnO Nanocolumnar (NC)

Sputtering → annealing

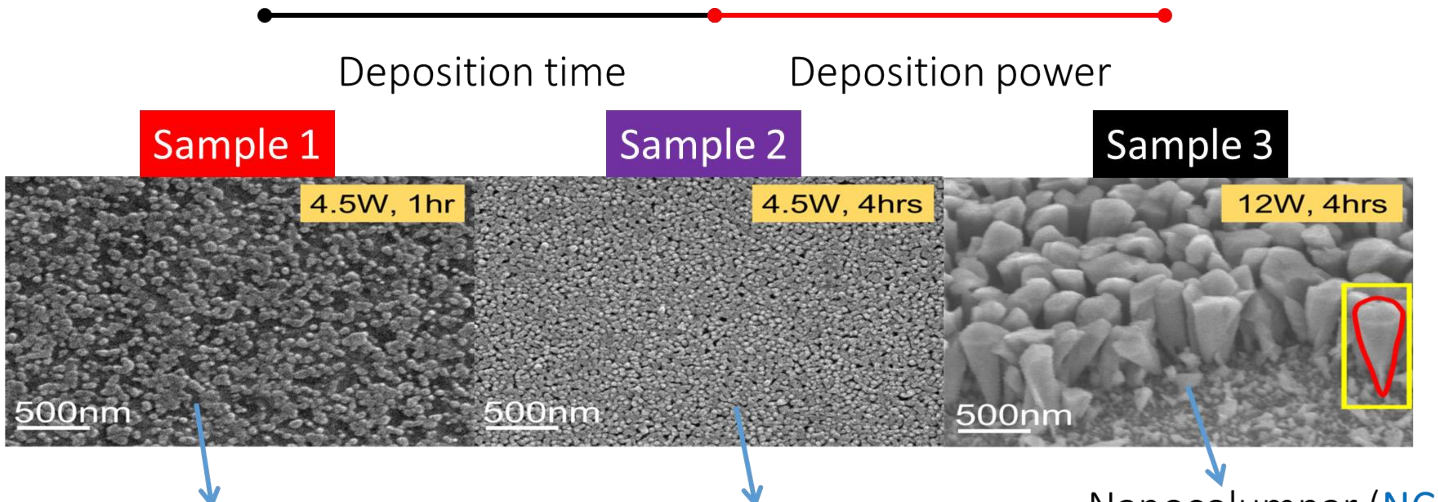
modification of magnetic and electronic properties of ZnO System

→Reduction of ZnO dimension to increase Zn vacancy at the surface

→ Ferromagnetic-Semiconductor (NC)

Magnetic properties of the ZnO

SEM images of ZnO under different deposition parameter



Deposition time

Deposition power

Sample 1

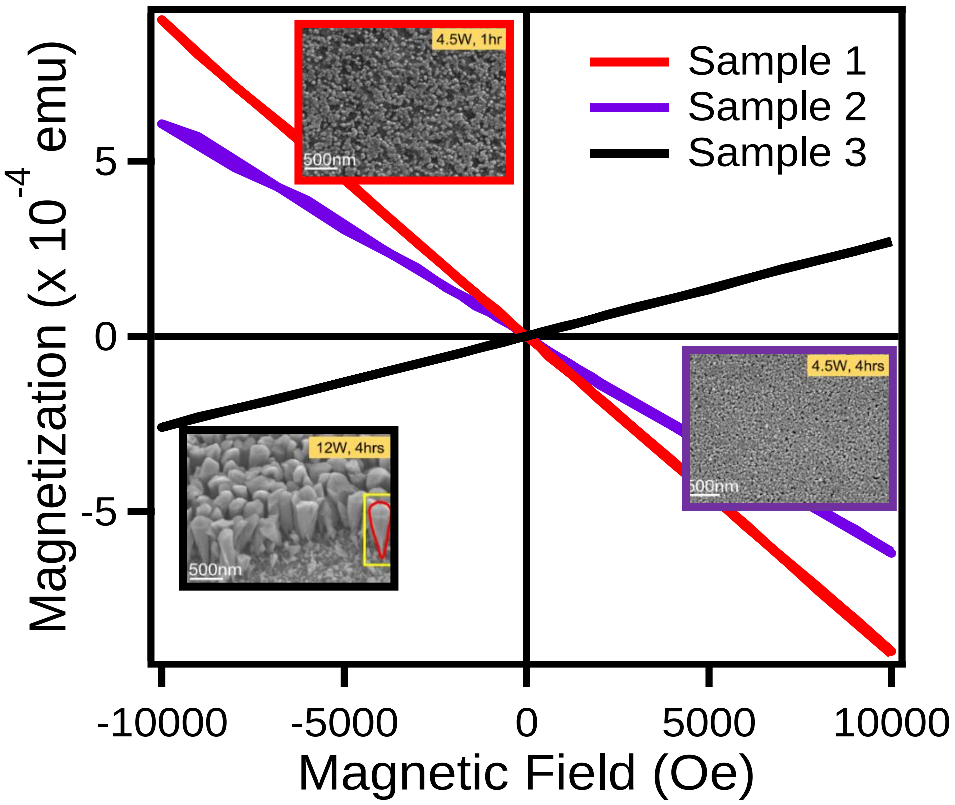
Sample 2

Sample 3

Inhomogeneous distribution

- Homogeneous distribution
- High density

Nanocolumnar (NC)



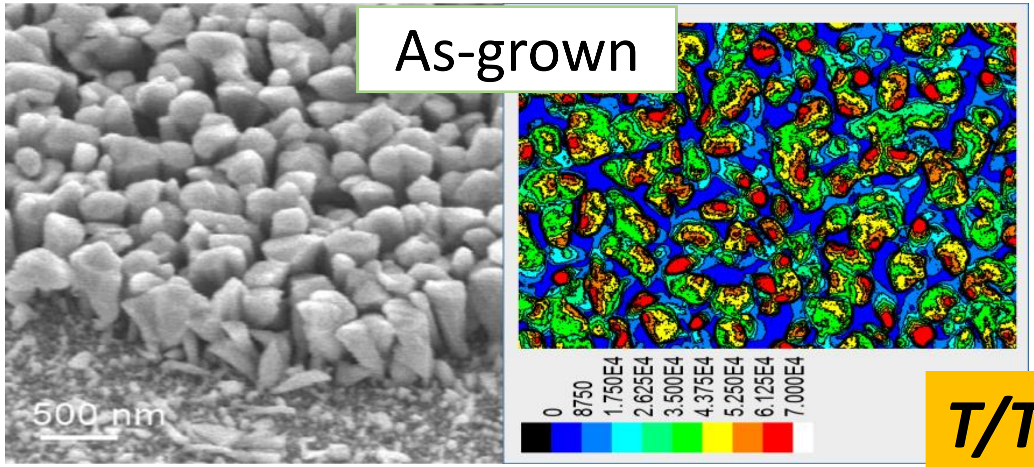
Sample 1 : diamagnetic

Sample 2 : diamagnetic

Sample 3 : paramagnetic

IEEE Magnetic Lett (2020) 11(1), 1-4, Art no. 2501704

Effects of thermal annealing on the structure of the ZnO NC

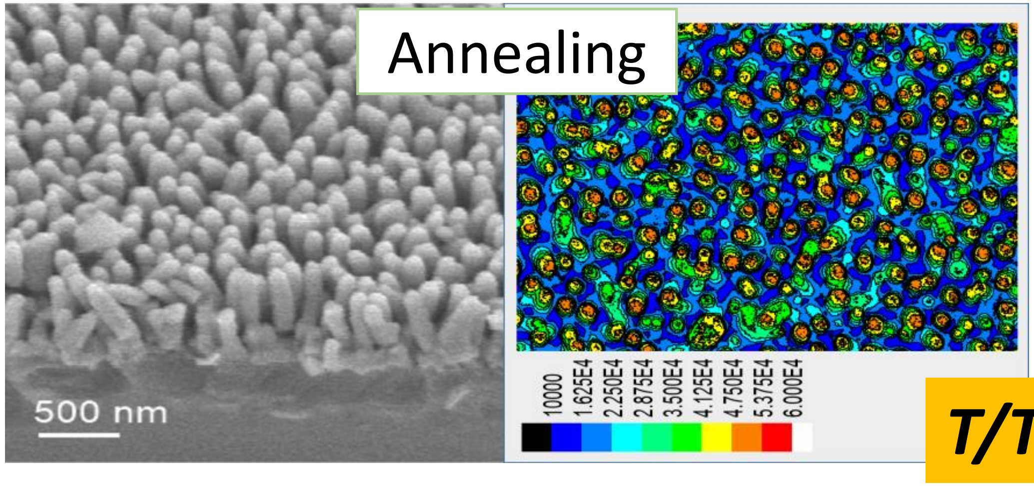


Non-uniformity of mass transfer during deposition

Promotes an inhomogeneous size along the vertical direction, forming a cone-like shape ($\boldsymbol{T/T_m}$~**0.2** zone I).

***T/T_m*~0.2**

Post-annealing at 600ºC + O_2

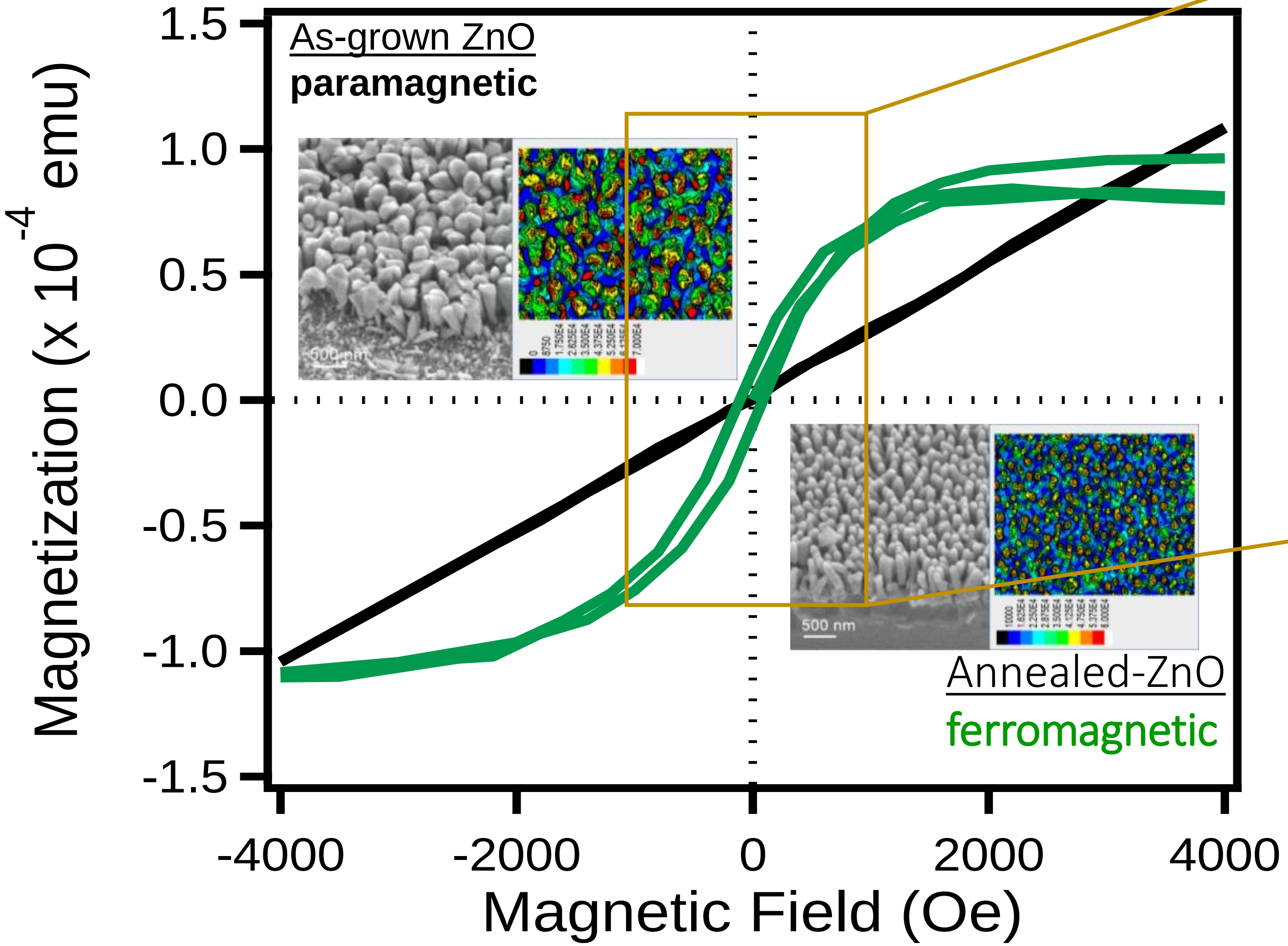


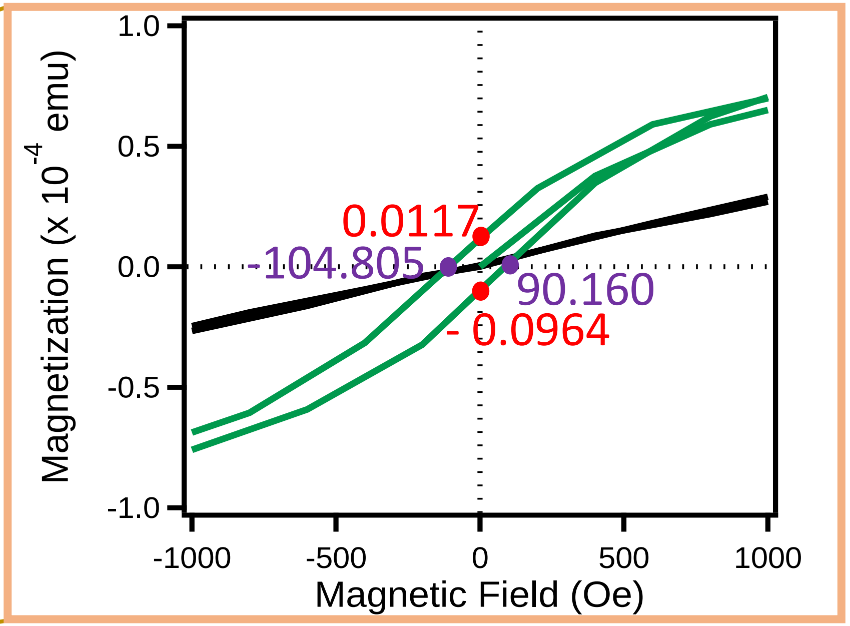
Post-annealing at 600ºC promotes structural change ($\boldsymbol{T/T_m}$~**0.3** zone II)

- ☐Structure changes from cone-like to rods shapes.
- ☐O_2 exposure promotes the decrease in thickness.

***T/T_m*~0.3**

Magnetization as a function of applied field





Properties	**As-grown ZnO**	**Annealed-ZnO**
+M_r (emu)	-	1.17×10^{-6}
-M_r (emu)	-	-9.64×10^{-6}
+H_c (Oe)	-	90.160
-H_c (Oe)	-	-104.805

❑ As-grown ZnO

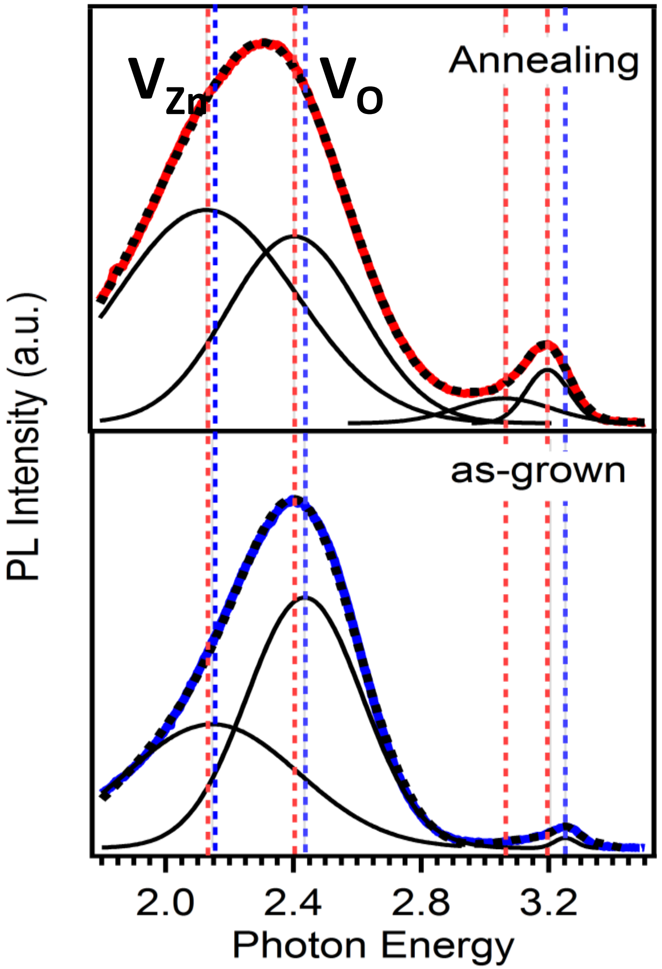
Linear line → **paramagnetic**

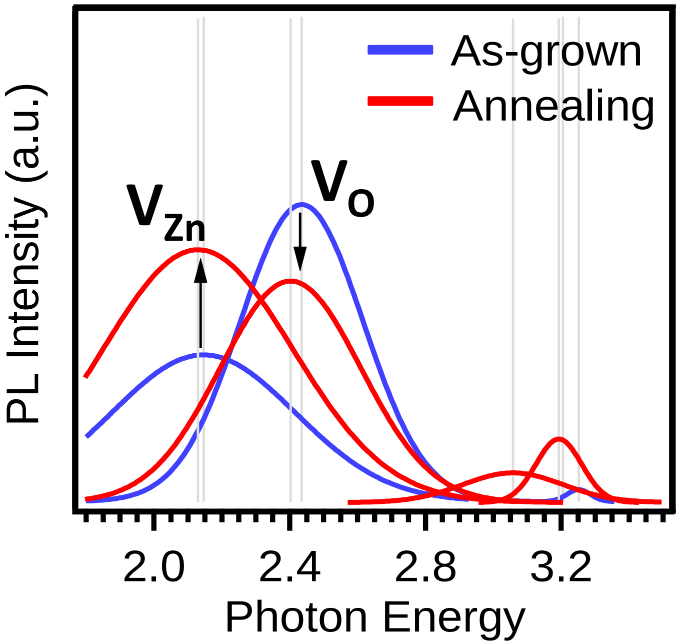
❑ Annealed-ZnO

“S” profile → **ferromagnetic**

Y. Darma et al, IEEE mag Let 2020

Photoluminescence spectra of the ZnO NCs





☐ <u>As-grown ZnO</u>

paramagnetic →

Domination of V_O defect

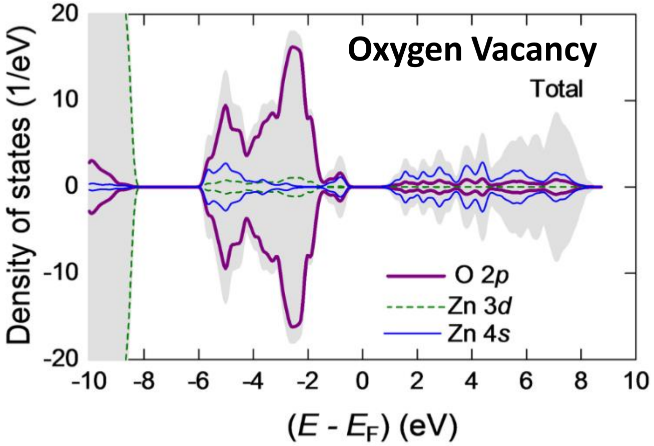
☐ <u>Annealed-ZnO</u>

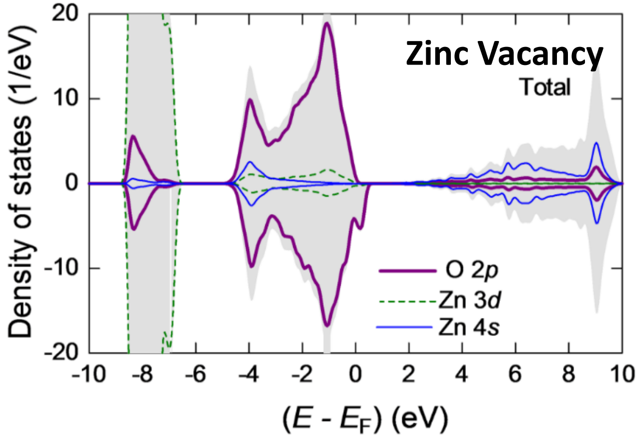
ferromagnetic →

Domination of V_{Zn} defect

IEEE Magnetic Lett (2020) 11(1), 1-4, Art no. 2501704

Density of States of the ZnO

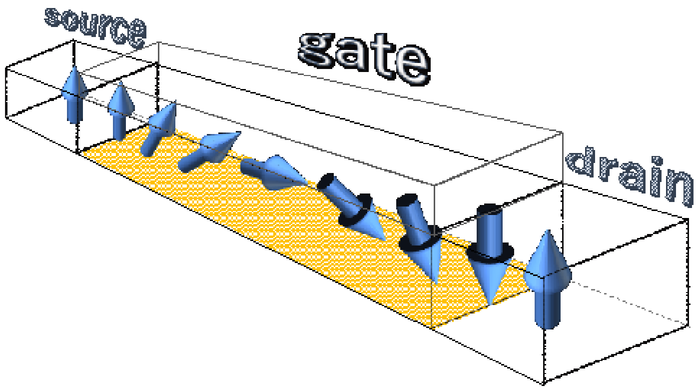


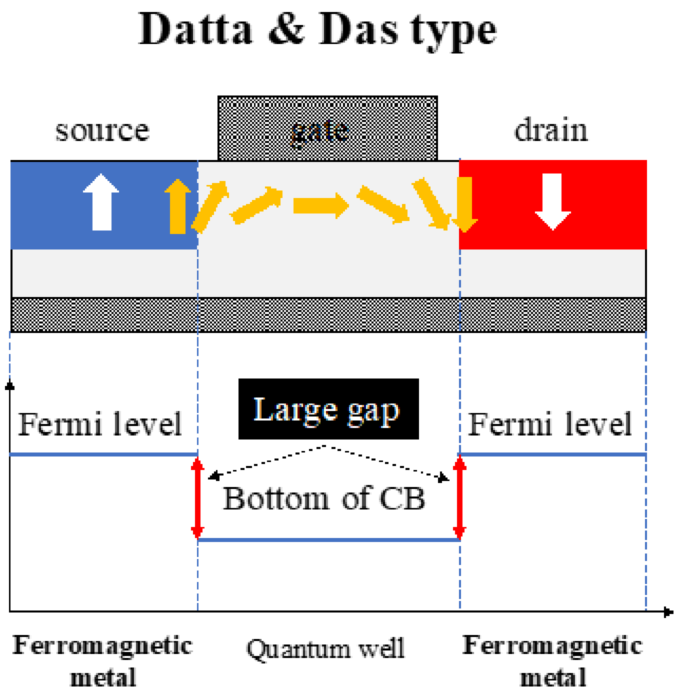


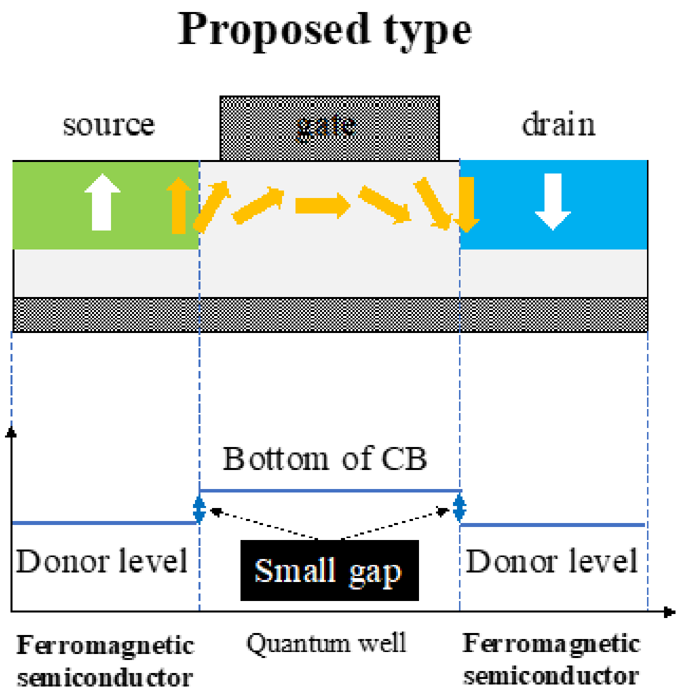
Zn vacancy (V_{Zn})-induced RT ferromagnetism

Ferromagnetic-Semiconductor ZnO for Spin FET

Spin Field Effect Transistor (FET)



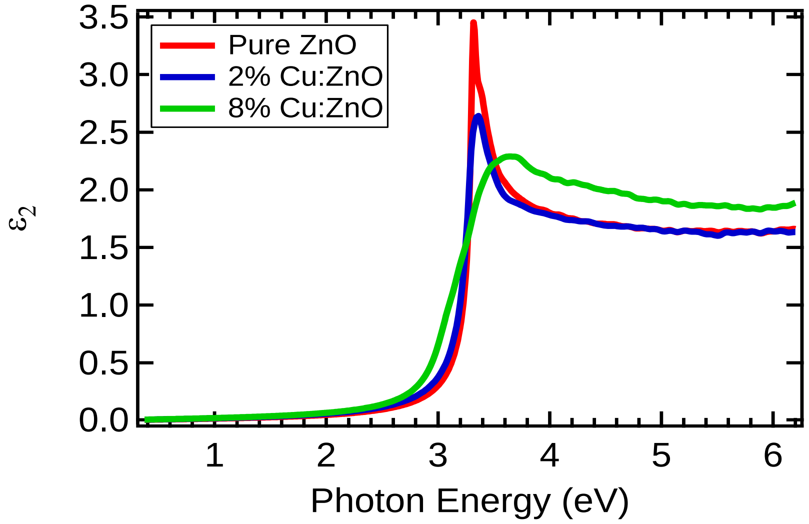




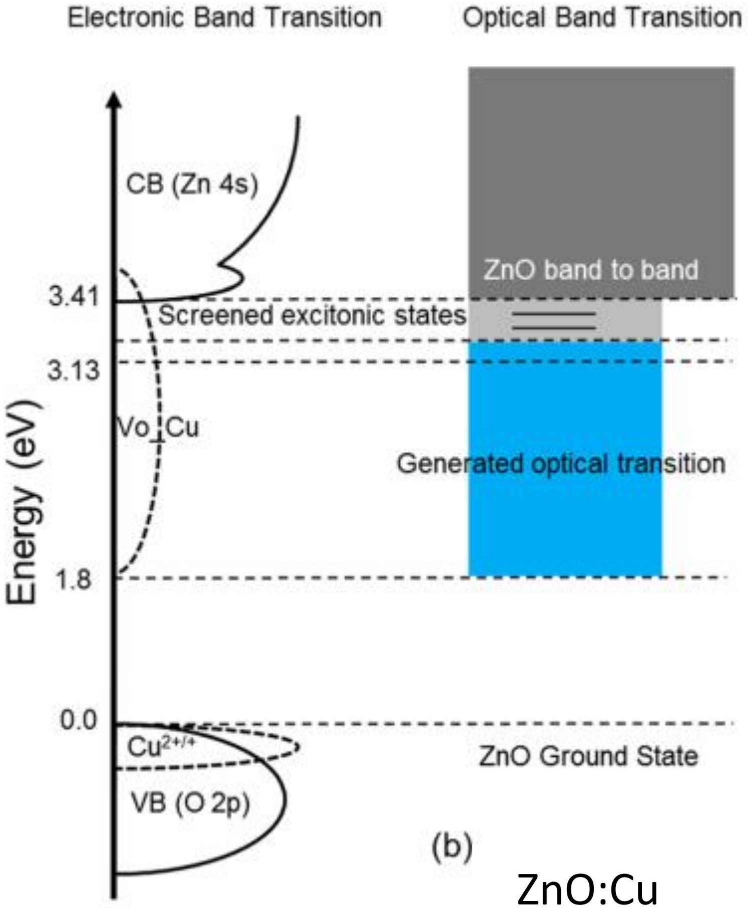
Appl. Phys. Lett. 56, 665, 1990

Ferromagnetic semiconductor is expected to play an important role as electrodes providing spin polarized electron in next generation device of spin FET

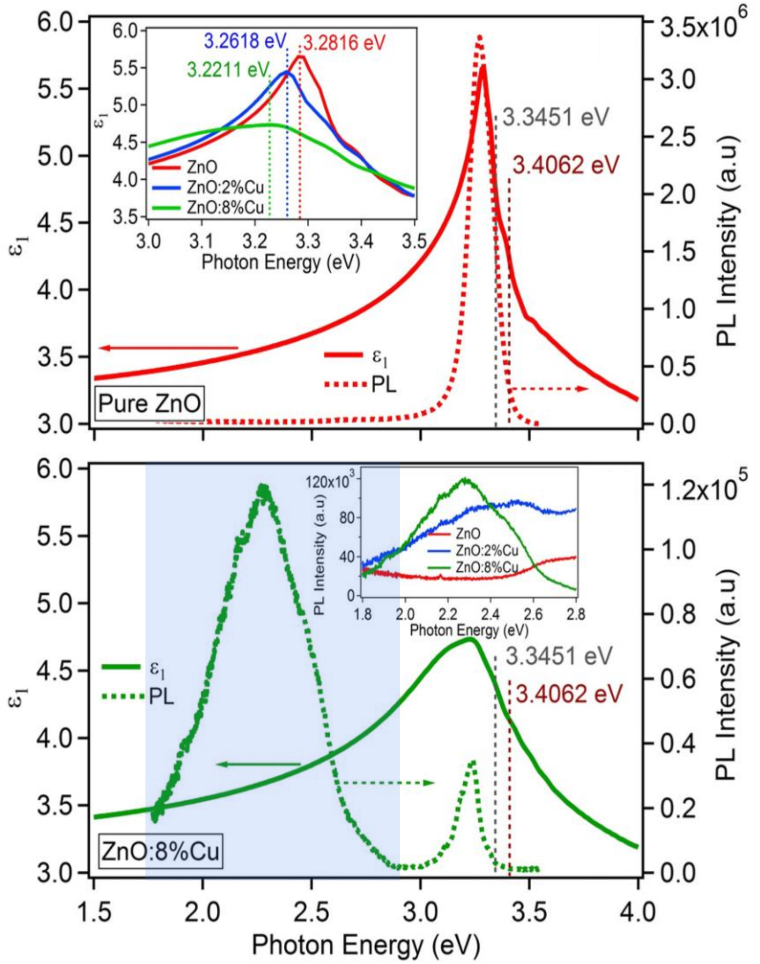
Doping; Exciton in ZnO:Cu



System with Cu impurities, a few quasi-free electrons may be provided by Cu $3d^9$. This leads to electronic screening effects and reduced the intensity of excitons.



ZnO:Cu

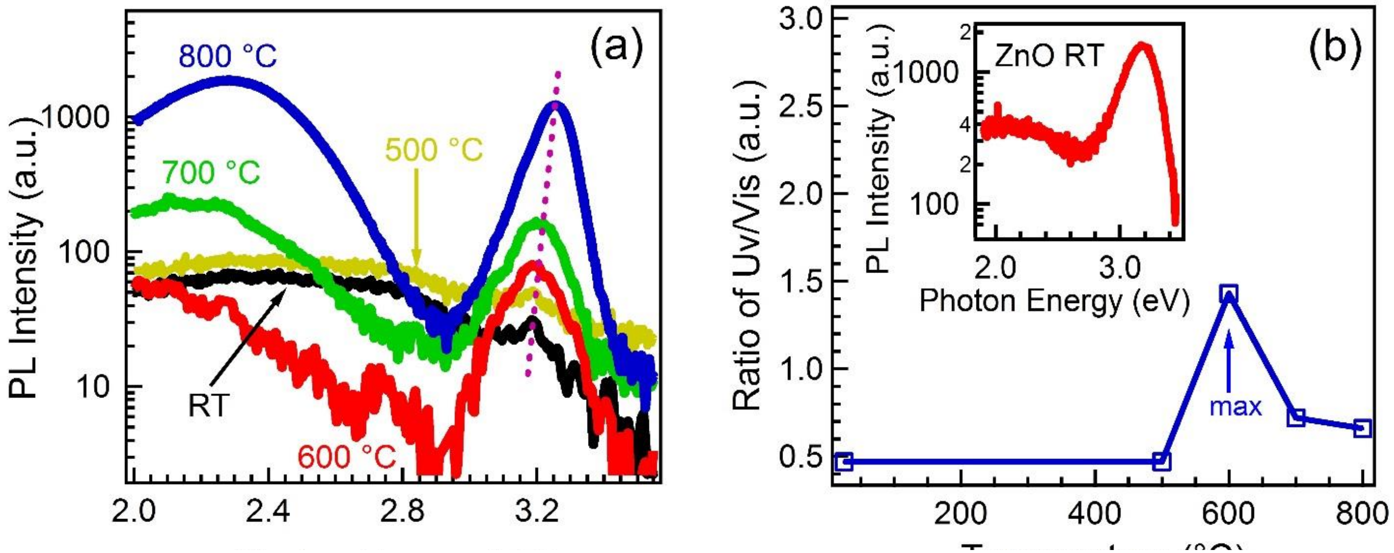


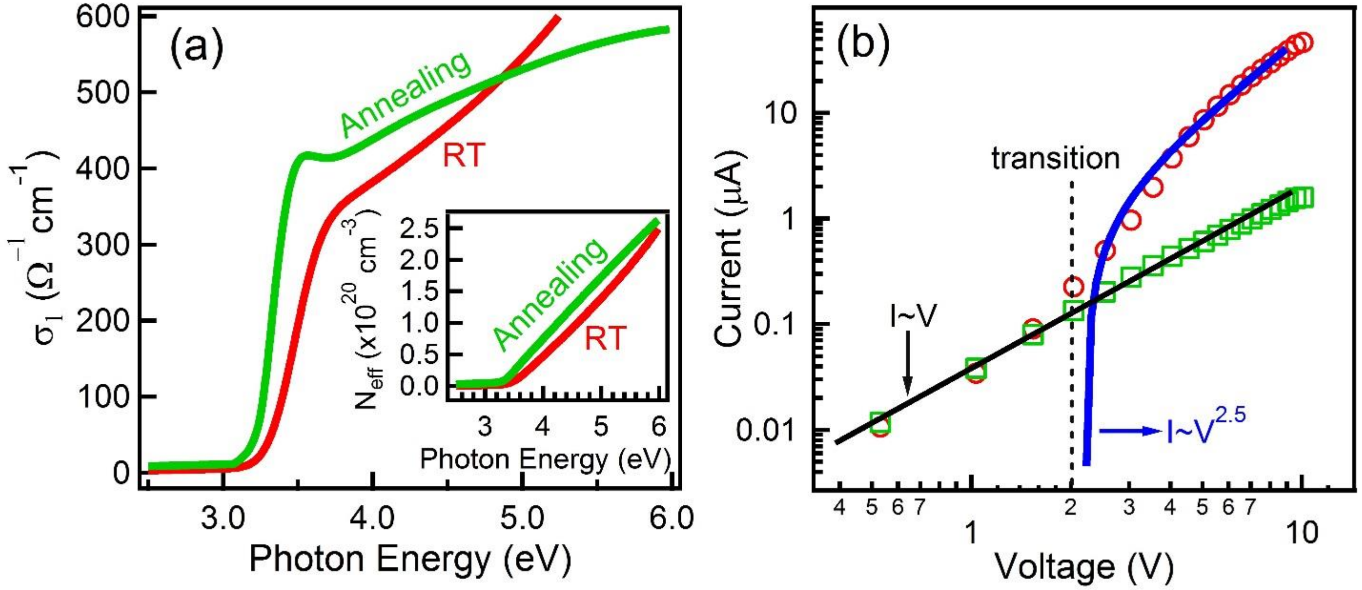
Interplay of Cu and V_O
→ mid-gap optical transitions

SE and PL techniques
→ powerful to detect defects bands and excitonic peaks

App. Phys. Lett. 104, 081922 (2014)

Doping; Effect of annealing temperature (ZnO:Ti)



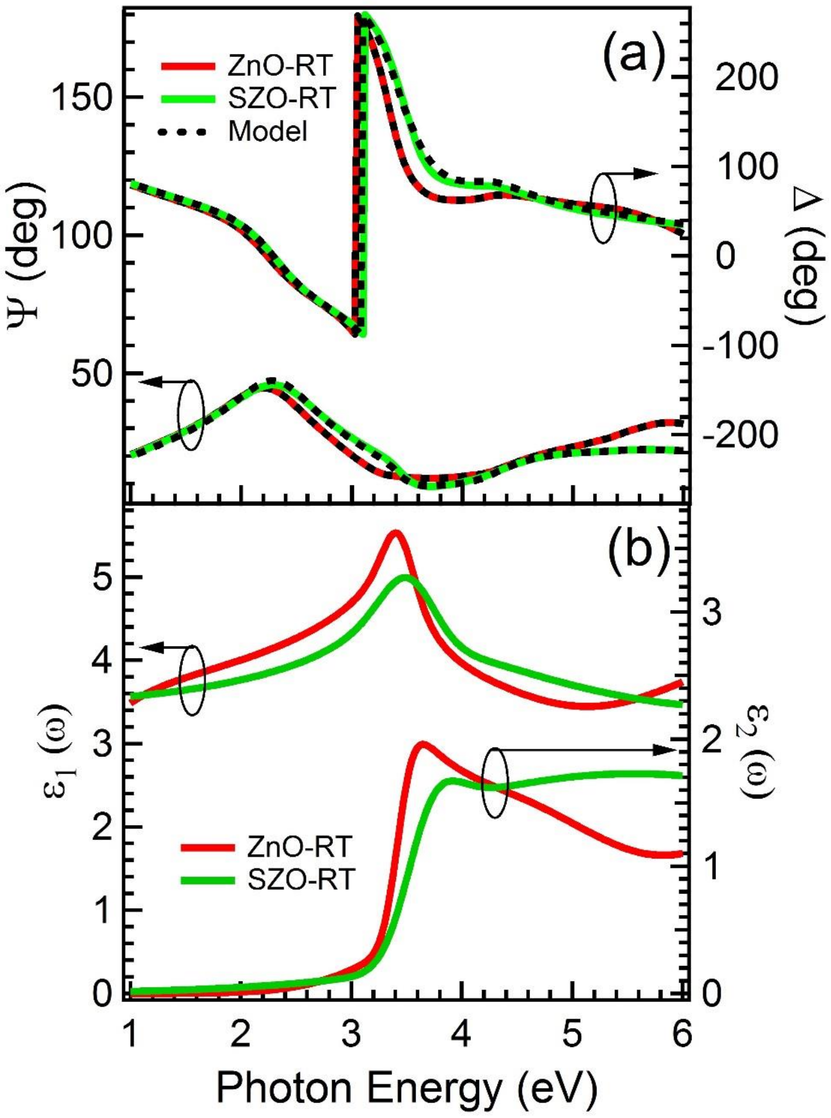


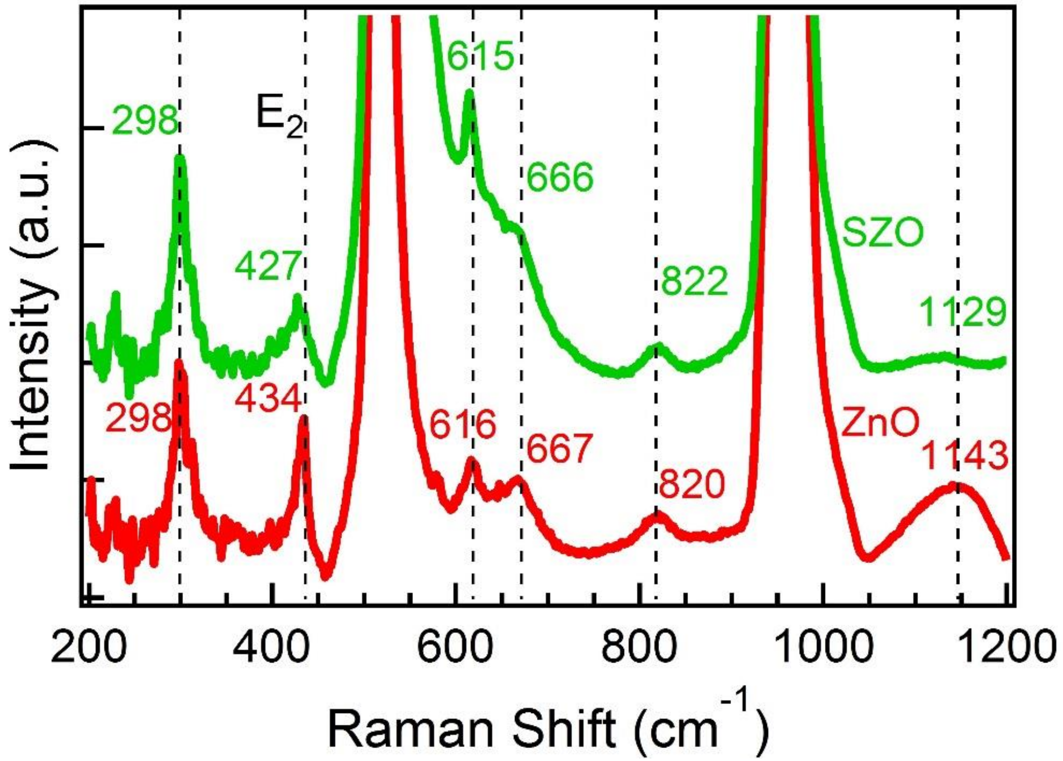
The contribution of oxygen vacancies
→ green emission (~2.5 eV)
→ electrical properties (space charge limited current regime)

Materials Research Express (2019) 6, 076434

Doping; Defects in ZnO:Sn Thin films

Sn dopant





Sn doping promotes the formation of oxygen vacancy-related trap states as indicated by A1 LO mode in Raman spectra and green emission in photoluminescence spectra.

Optical Materials (2019) 88, 111-116

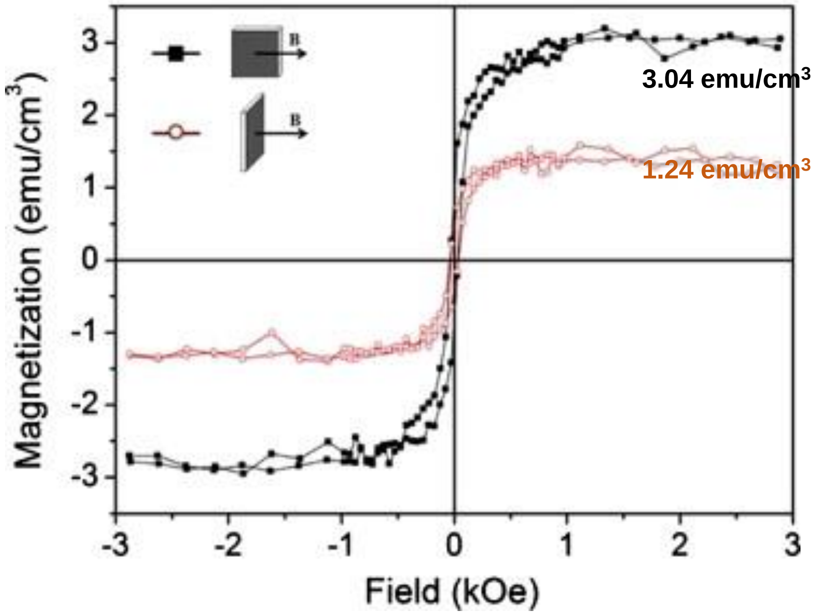
Carbon-doped ZnO

properties → Optimized → **Dopant**

Properties:
- room temperature ferromagnetic response
- hybridization of Zn and C ions
- an important role in polarization and optical characteristic

However, no report on the polarization characteristic of C-doped ZnO

The Ferromagnetism of ZnO:C



C.S.Wei., et al., Appl. Surface Science, Vol. 258, No. 14, 2012

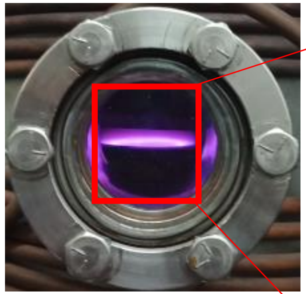
→ **investigate the polarization and optical behavior in C-doped ZnO nanocolumnar structure, which has high polarity.**

Ex: Sample preparation and characterizations

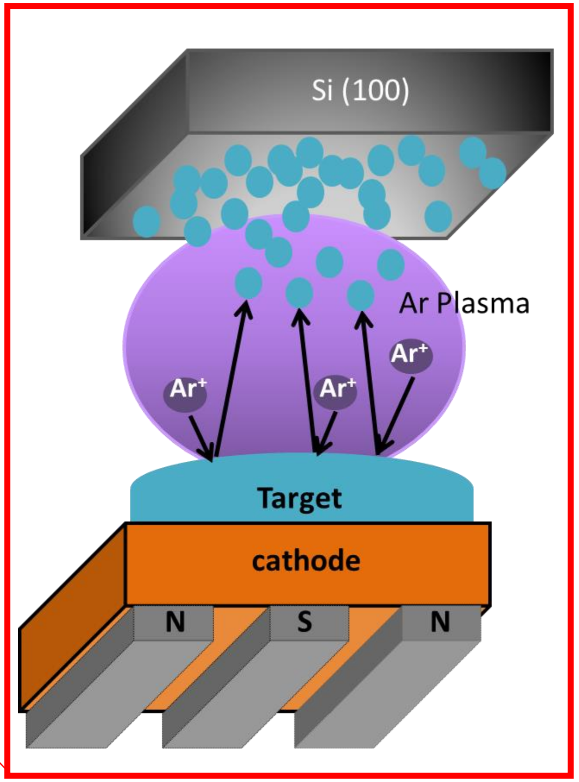
Sputtering target

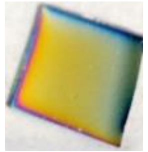
Substrate preparation

Deposition process :
DC-unbulance magnetron sputtering



Parameters;
t= 4 hours,
$T_{substrat}$= 300 ^{0}C
P=0.3 kPa,
Power= 12 W



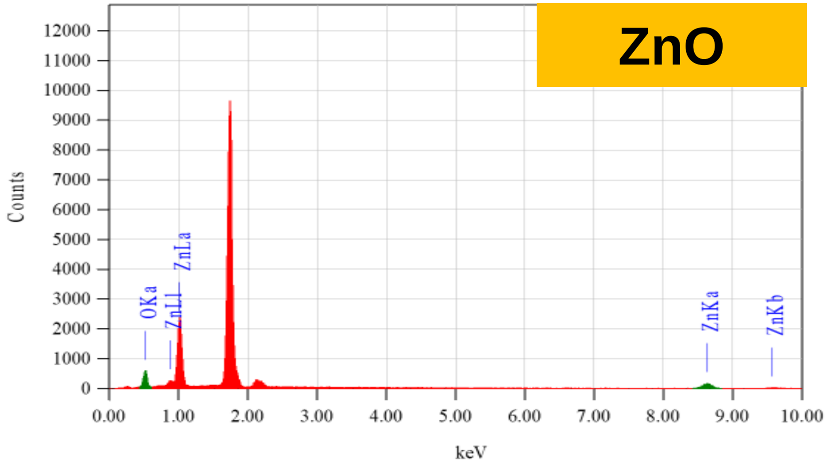


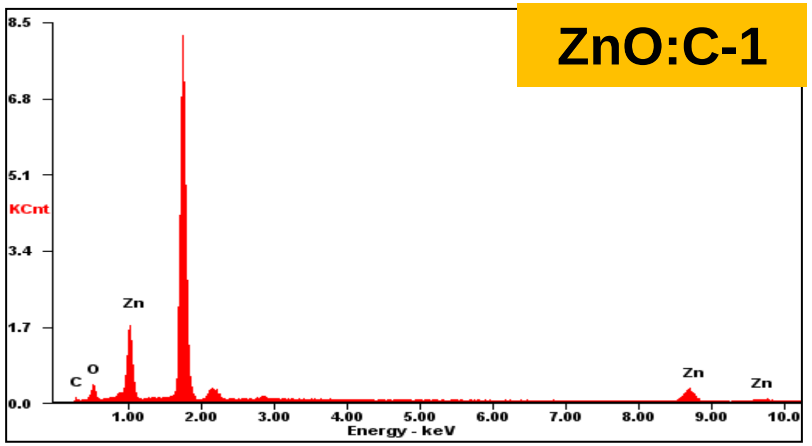
- ☐ **ZnO**
- ☐ **ZnO:C-1**
- ☐ **ZnO:C-2**

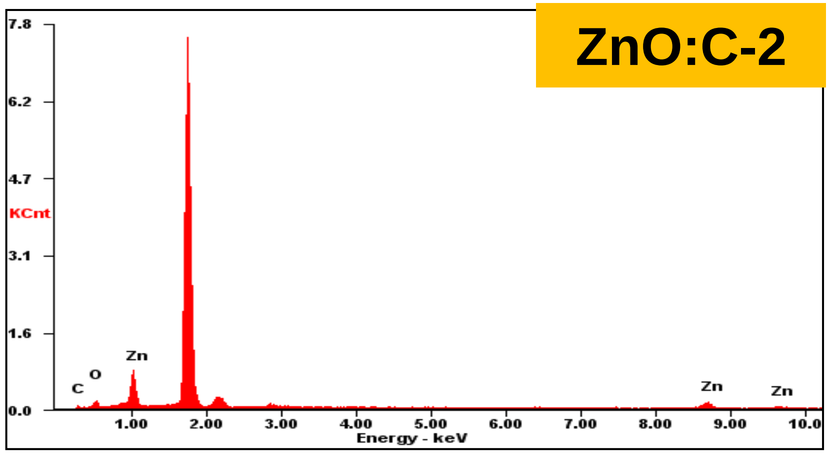
Characterizations:

FESEM, EDX, XRD, RT66A ferroelectric test system, PL, and UV-Vis.

Results and Discussions: EDX Spectroscopy


ZnO

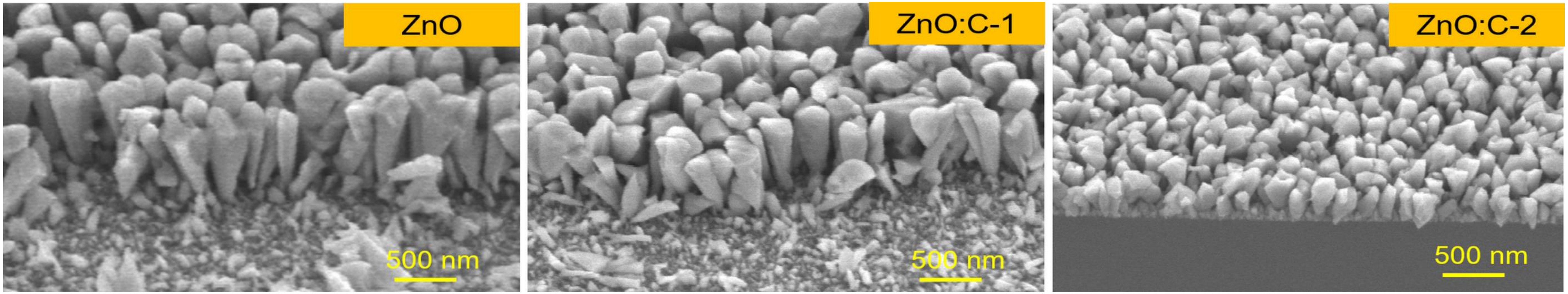

ZnO:C-1


ZnO:C-2

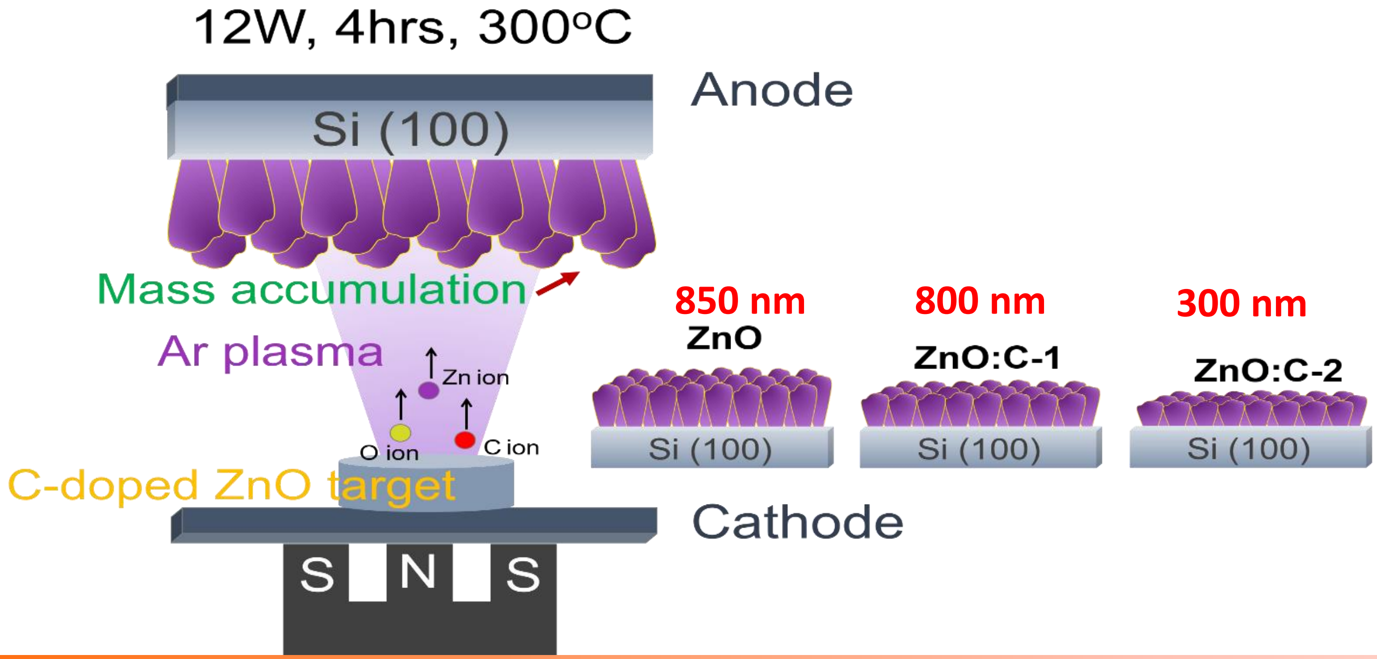
Sample name	Atomic concentration (%)			Total (%)
	Zn	O	C	
ZnO	36.86	63.14	0	100
ZnO:C-1	40.05	47.52	**12.43**	100
ZnO:C-2	30.38	37.86	**31.76**	100

The C atom is successfully doped with ZnO

Surface morphology



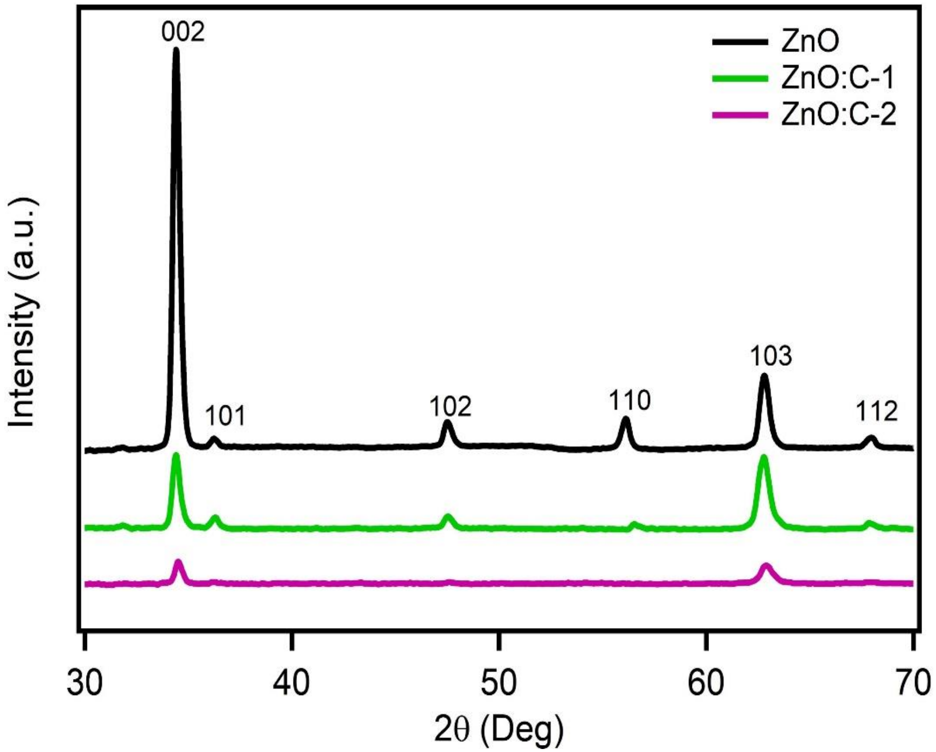
Hendri,et al.,(2022). **Ceramics International**, 48(2), 2038-2044.



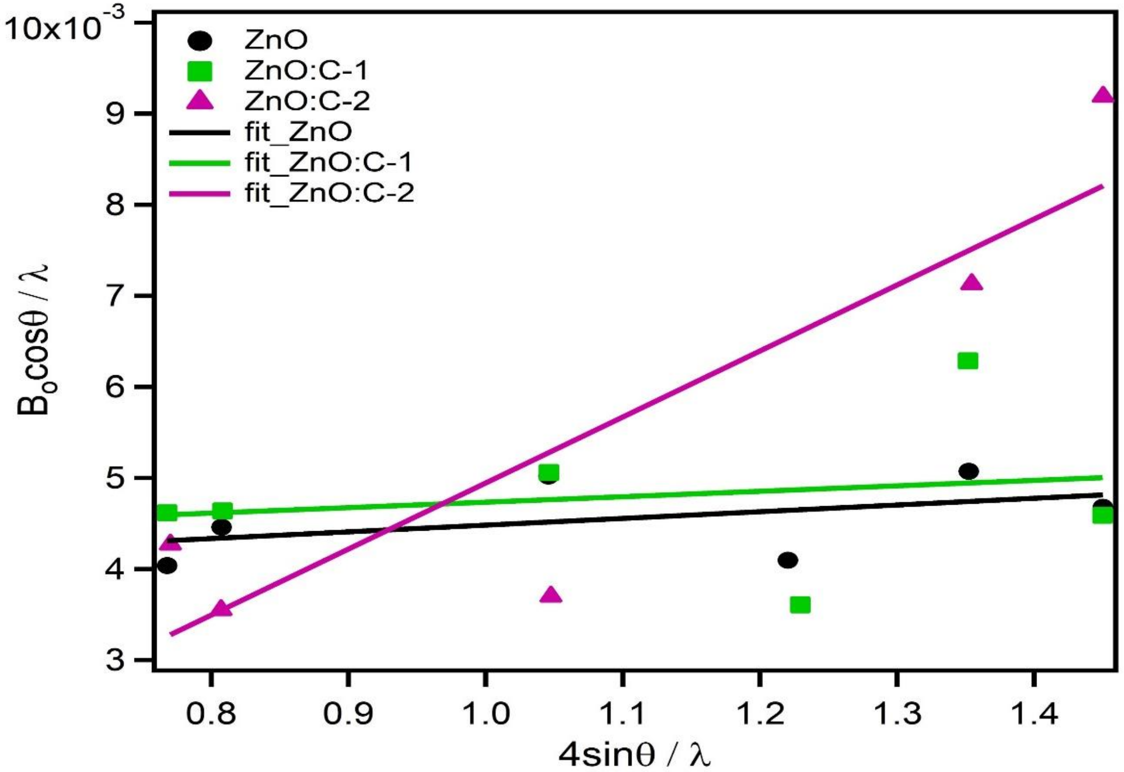
The smallest thickness of C-doped ZnO NCs by increasing the C concentration due to the different sizes of C, Zn, and O atoms will increase the chance of collisions between the atoms and affect the mean free path of the atoms.

Crystal structural

XRD pattern

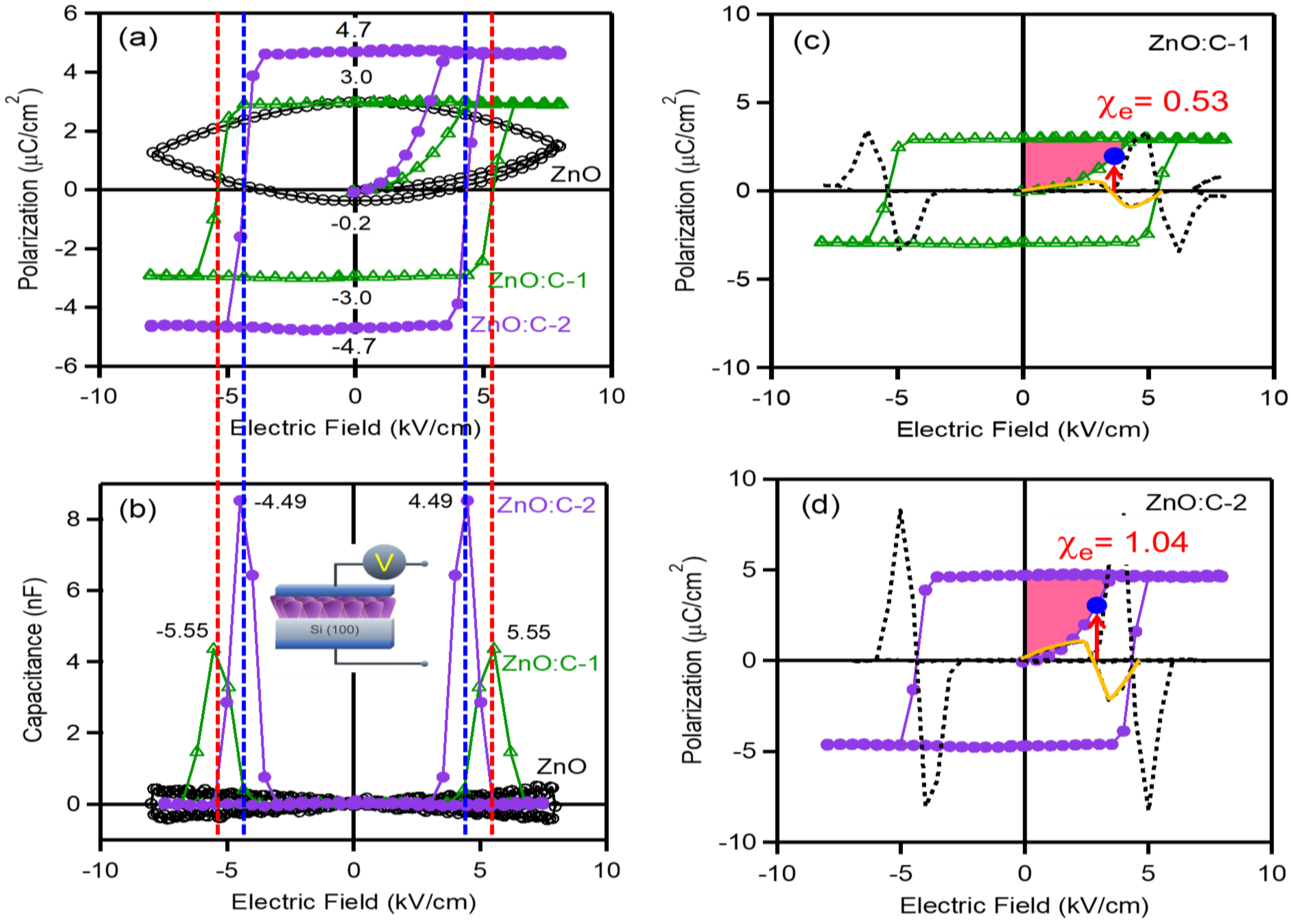


Williamson-Hall plot



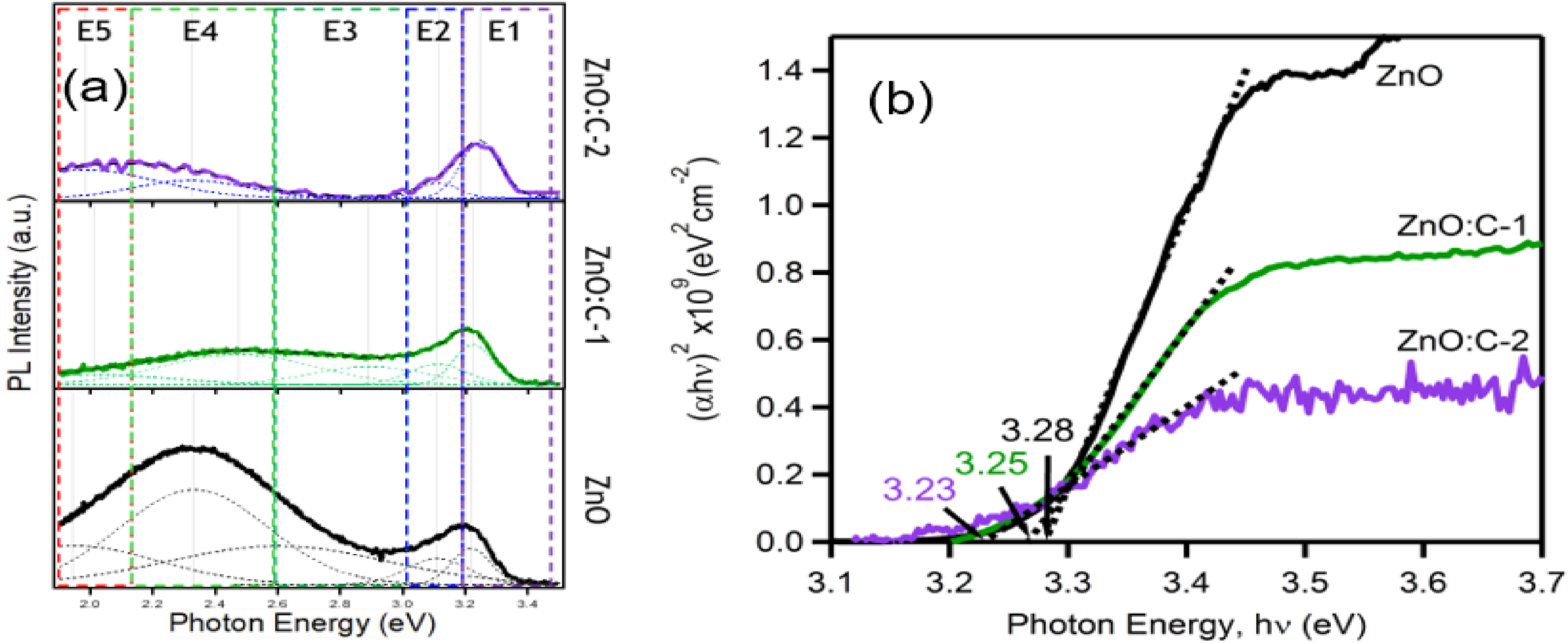
The increase of carbon concentration led to increase of lattice strain (ε) and decrease of crystallinity in dominant at (002) peak intensity.

Polarization and capacitance



The ferroelectric characteristics of the material are indicated by the butterfly capacitance curve with the sharp switching point, which indicates the change of polarity

Photoluminescence and absorption spectra



- ❑ The addition carbon in ZnO leads the increase in NBE emission accompanied by decreasing in defects emission
- ❑ The increase of carbon concentration promotes the decrease in absorption intensity accompanied by the red shift

List table of emission of the C-doped ZnO NCs

Sample name	Emission	Description
ZnO	E1 (3.219eV) E2 (3.111eV) E3 (2.600eV) E4 (2.333eV) E5 (1.946eV)	E1: near-band-edge (NBE) emission E2: transition from Zn_i to valence band E3: transition from Zn_i to V_{Zn} E4: transition from V_O* to valence band / V_{Zn} emission E5: transition from conduction band to V_O^{++}
ZnO:C-1	E1 (3.222eV) E2 (3.109eV) E3 (2.890eV) E4 (2.473eV) E5 (2.015eV)	
ZnO:C-2	E1 (3.245eV) E2 (3.112eV) E4 (2.323eV) E5 (1.986eV)	

Thank you