Spectroscopy and ab initio studies of optical transitions in nanostructured ZnO

R. Plugaru[a)], A. Dinescu[a)], F. Comanescu[a)], M. Purica[a)], S. Mihaiu[b)], E. Vasile[c)], F. Babarada[d)], N. Plugaru[e)]

[a)] National Institute for Research and Development in Microtechnologies-IMT Bucharest

[b)] Institute of Physical Chemistry "I.G. Murgulescu" Romanian Academy

[c)] METAV S.A.-CD, Bucharest

[d)] University “Politehnica” Bucharest

[e)]National Institute for Materials Physics, Bucharest-Magurele

Project 11-048/2007 NANOXI

Layout

- Overview
- Experimetal
  - Synthesis
  - XRD, SEM, TEM
  - UV-VIS and Fluorescence Spectroscopy
- DFT study
- Conclusions

Overview

- **ZnO (wide, direct band gap: E_g 3.2–3.4 eV at 300K) potential applications: transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin film transistors, optoelectronic and piezoelectric applications in surface acoustic wave devices.**

- **Al doping in ZnO : reported to change the electrical and optical properties of ZnO thin films. The influence of Al-doping on the visible light emission need to be further studied.**

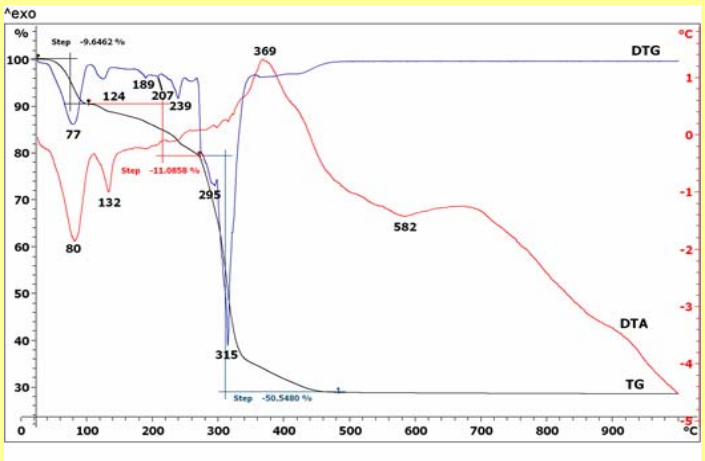
- **Strong interest in ZnO -based DMS : 3d transition metal (TM) doped bulk and films exhibit magnetic order at RT, with applications in spintronic devices, such as SLED (spin light-emitting diode) and SFET (spin field effect transistor). The doping process leads to maipulation not only of optical and electrical properties, but also to magnetic effects.**

Synthesis of ZnO:Al layers (0.5% and 5%Al)

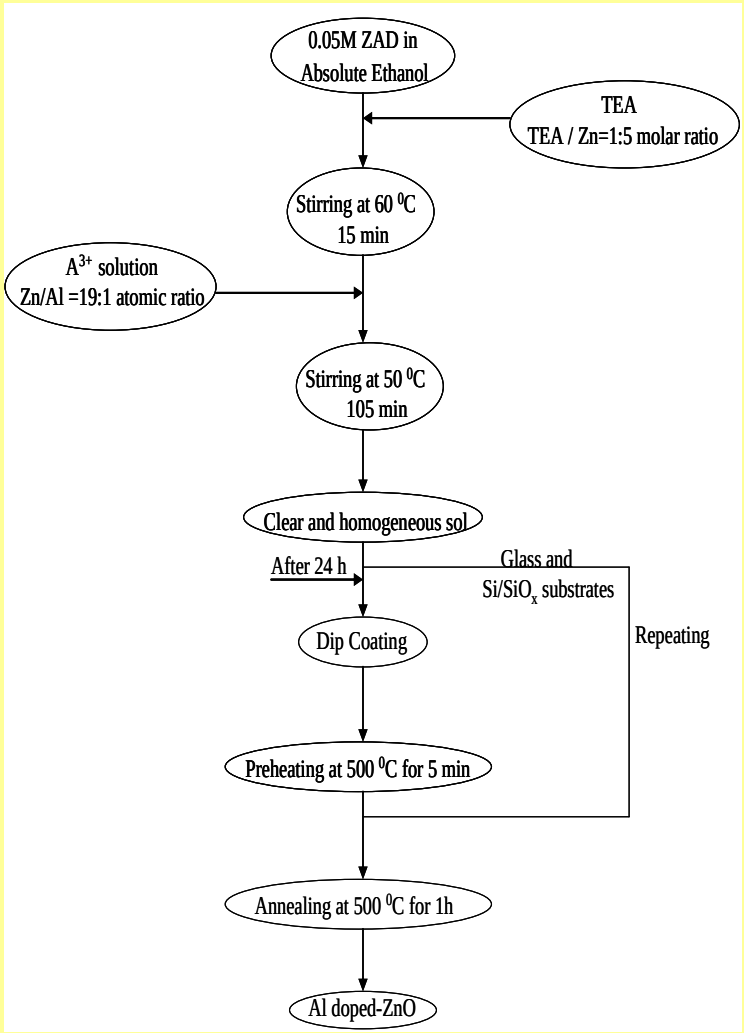
- **Sol-gel method on Si/SiO_2 and glass.**
- **Multilayers : n = 1 - 10 layers**
- **Thickness: ~10 nm/ layer**

Solutions prepared from:

- **Zinc acetate dihydrate (p.a):**
  $Zn(CH_3COO)2x2H_2O$ (ZAD)
- **Aluminiumnitrat-nonahydrat:**
  $Al(NO_3)_3 \cdot 9H_2O$(ANN)
- **absolute ethanol - CH_3CH_2OH**
- **Triethanolamine - $(CH_3CH_2OH)3N$ (TEA)**

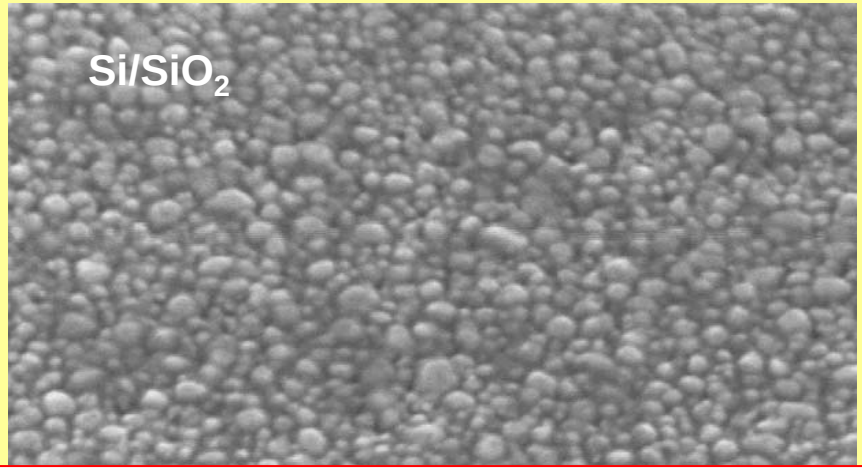


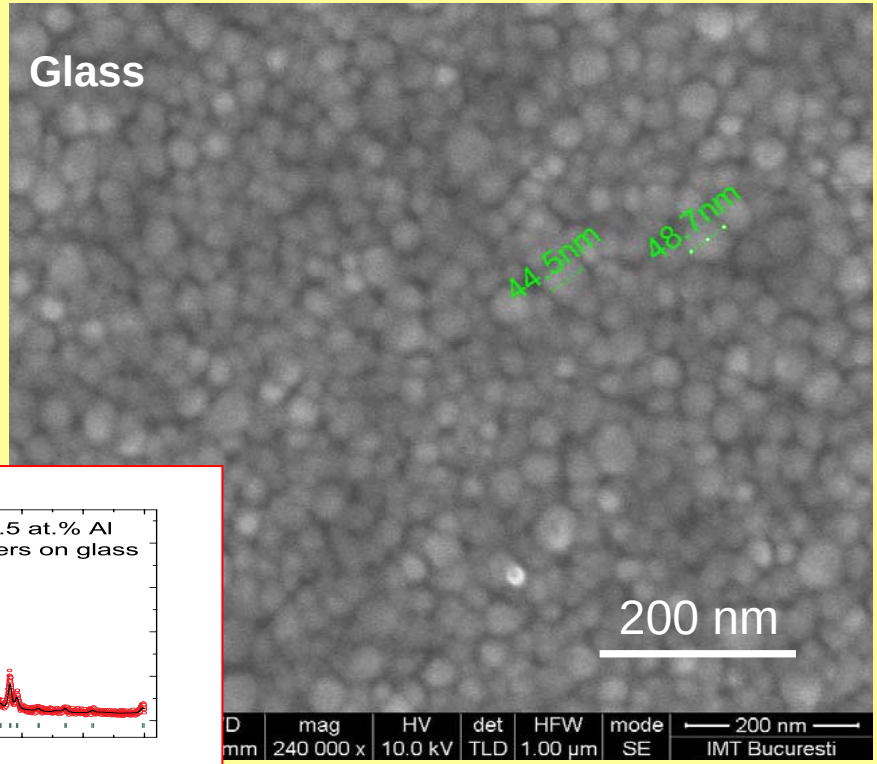
DTG, DTA and TG analysis of Al doped ZnO gel.

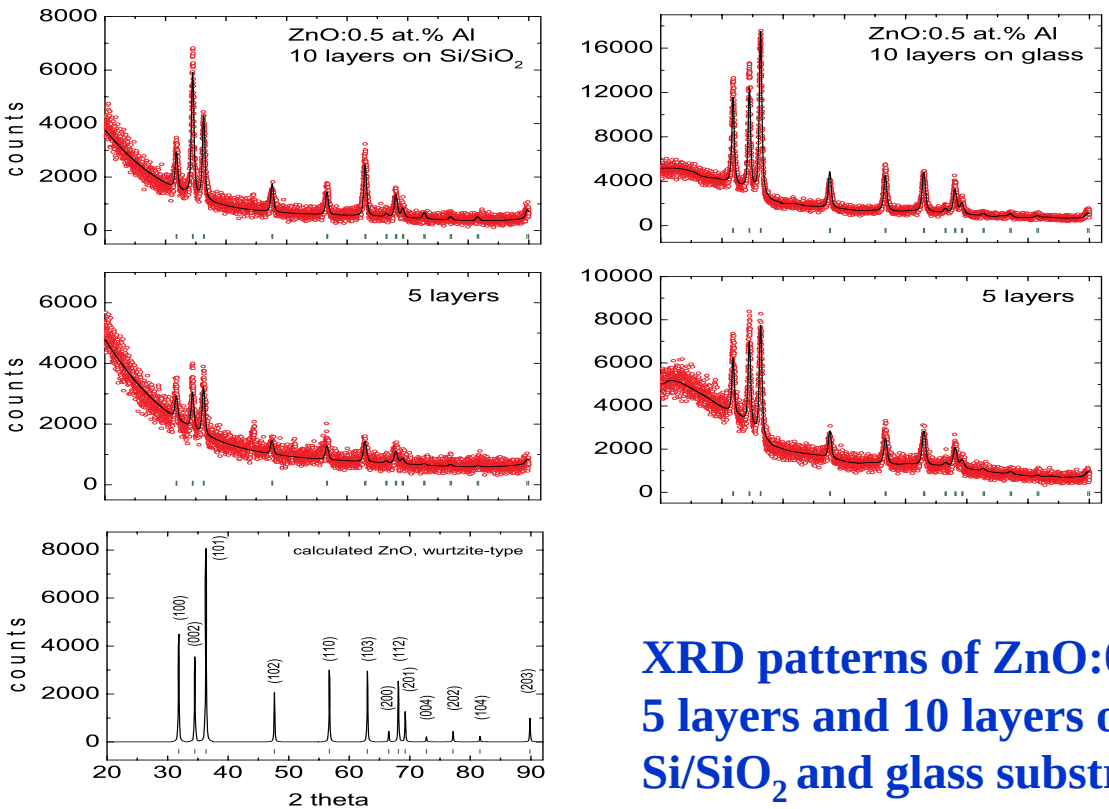


Preparation procedure of ZnO:Al multilayers by sol-gel process.

XRD and SEM



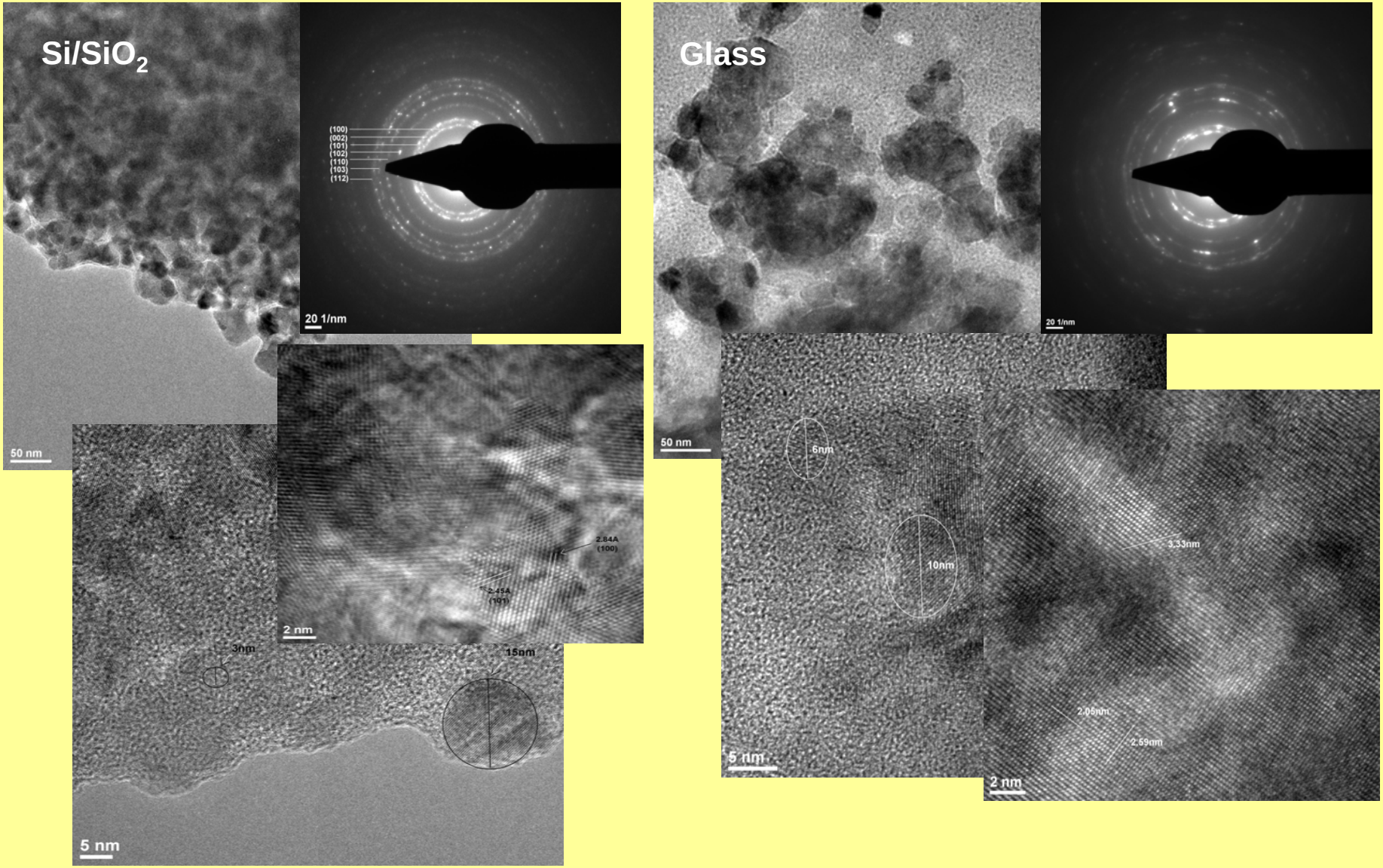




SEM images of the surface of ZnO:0.5%Al 10 layers films grown on Si/SiO_2 and glass substrates.

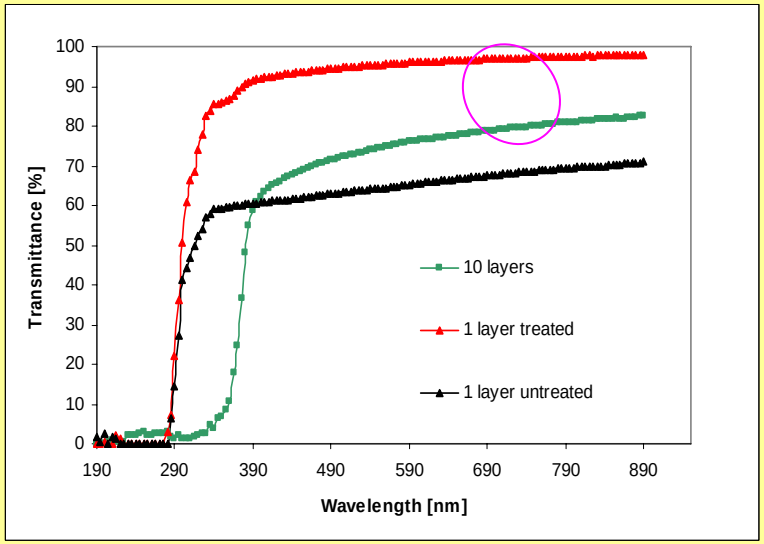
XRD patterns of ZnO:0.5%Al, 5 layers and 10 layers on Si/SiO_2 and glass substrates.

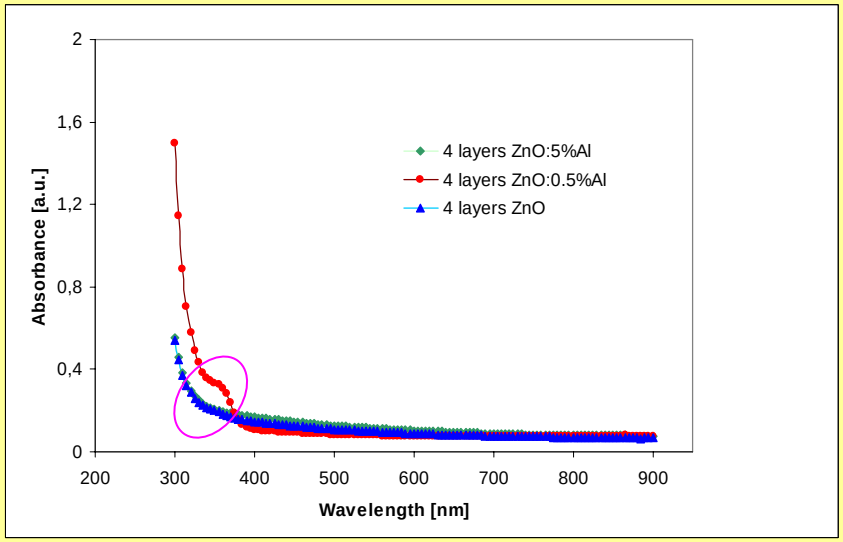
HRTEM

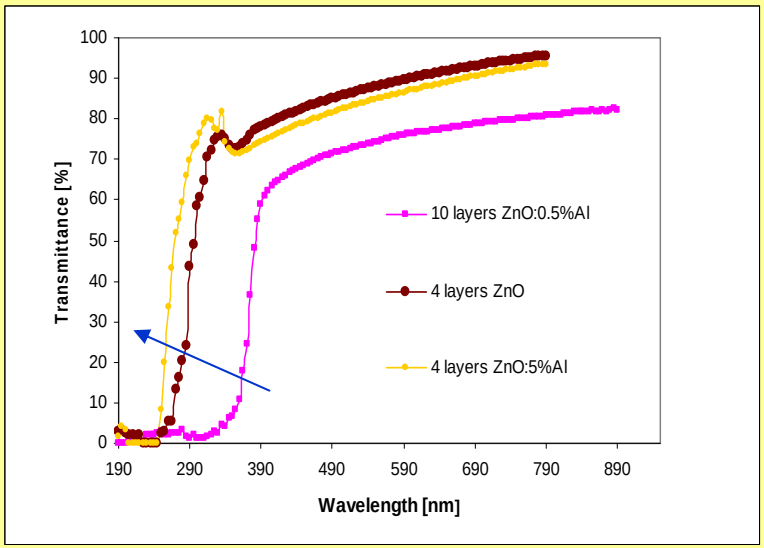


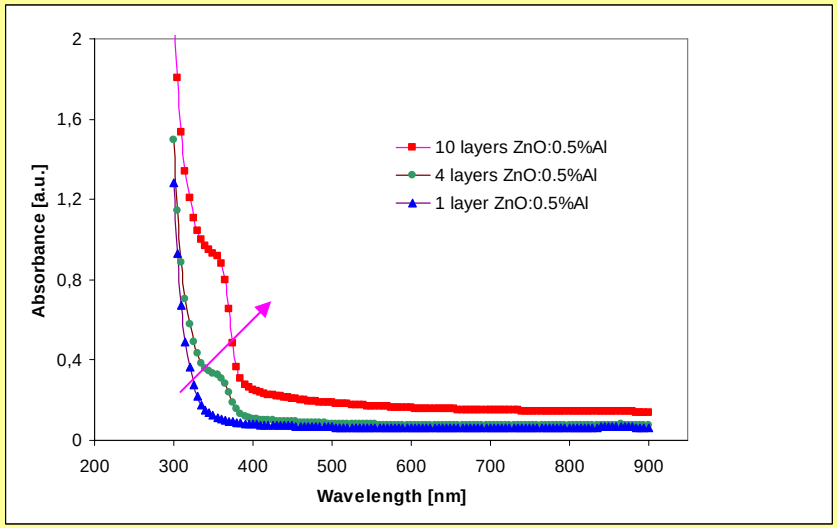
HRTEM images and corresponding SAED patterns of ZnO:0.5%Al 10 layers films grown on Si/SiO_2 and glass substrates.

UV-VIS Spectroscopy





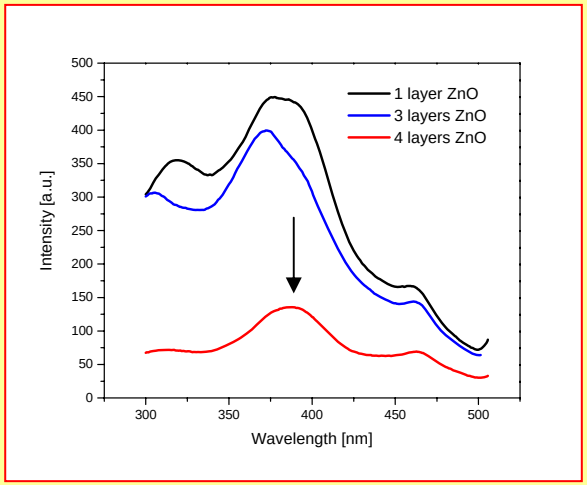


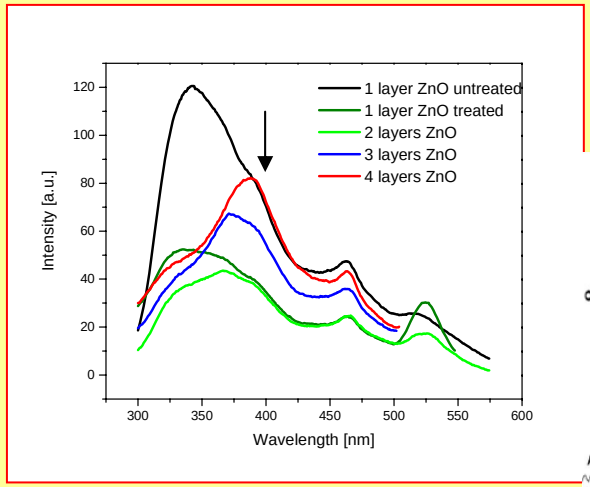


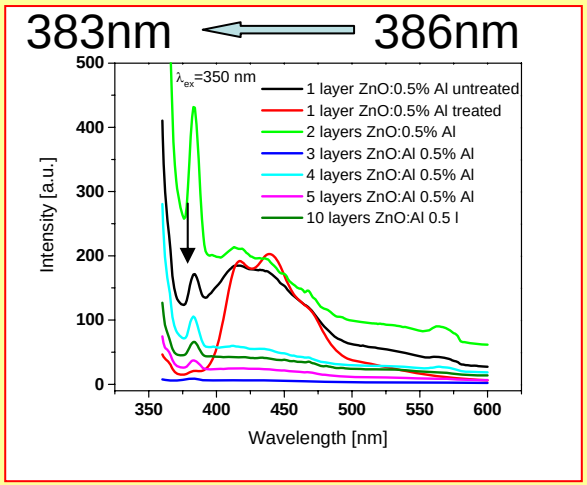
Optical transmission of ZnO, ZnO:0.5%Al and ZnO:5% Al layers.

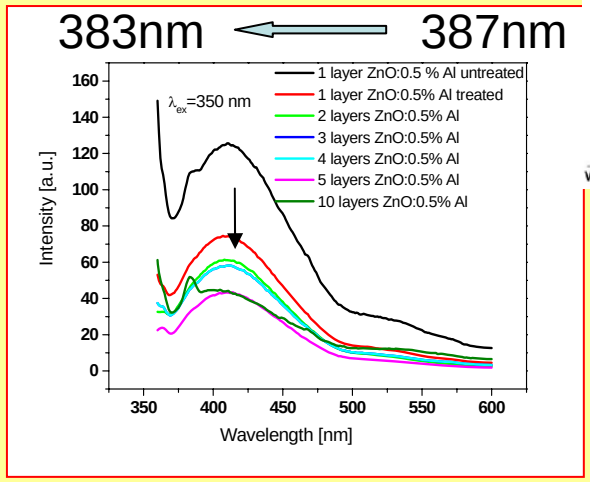
UV–VIS absorption spectra of ZnO, ZnO:0.5%Al and ZnO:5%Al layers.

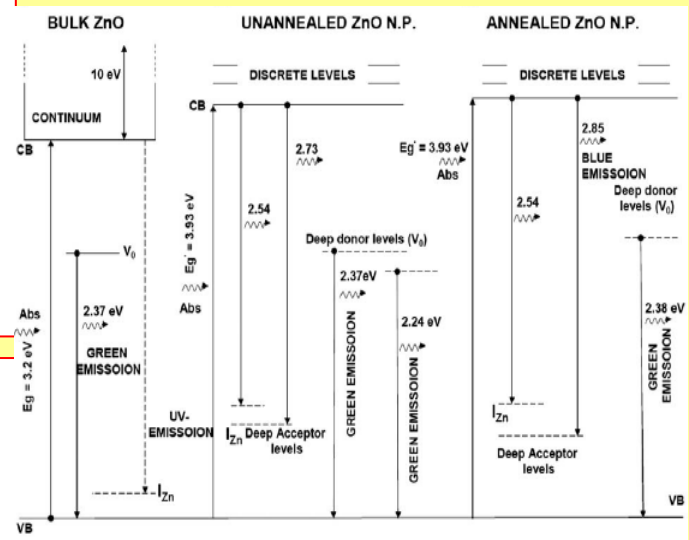
Fluorescence









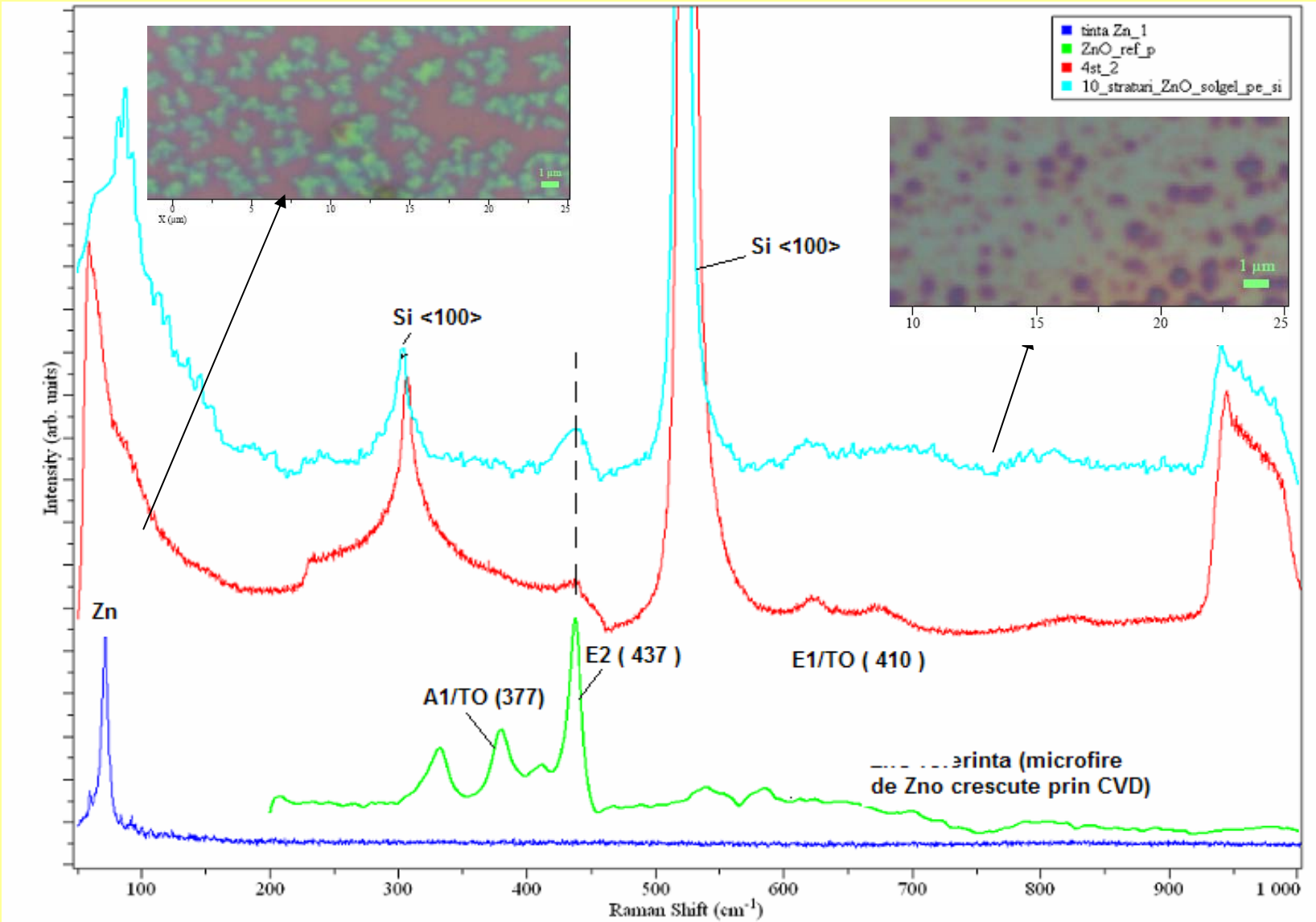


Absorption and fluorescence emission in the bulk ZnO and nc ZnO.

[N. Goswami, D.K. Sharma / Physica E 42 (2010) 1675–1682]

Fluorescence properties of ZnO and ZnO:0.5%Al layers grown on Si/SiO_2 and glass substrates, at an excitation wavelength of 350 nm.

Raman Spectroscopy

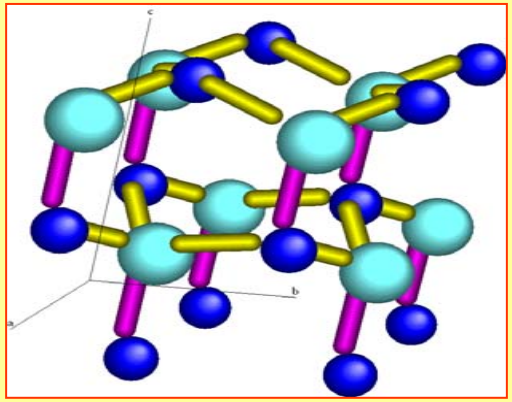


Micro-Raman LabRAM HR 800/HORIBA

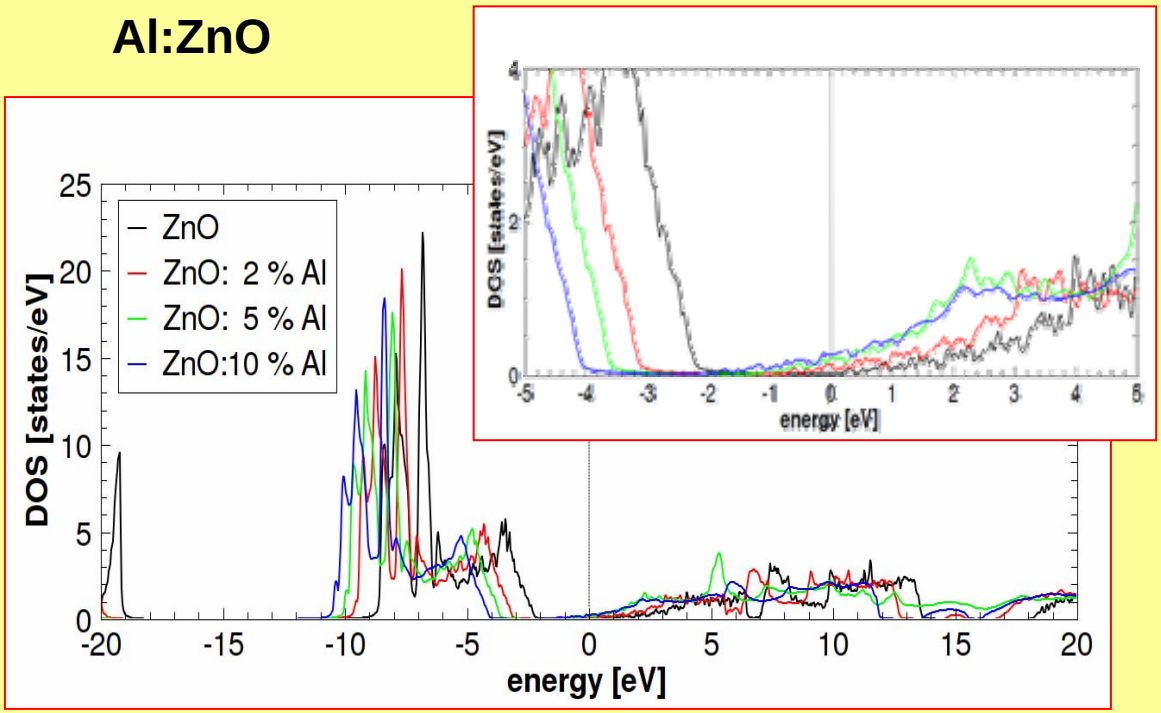
DFT study

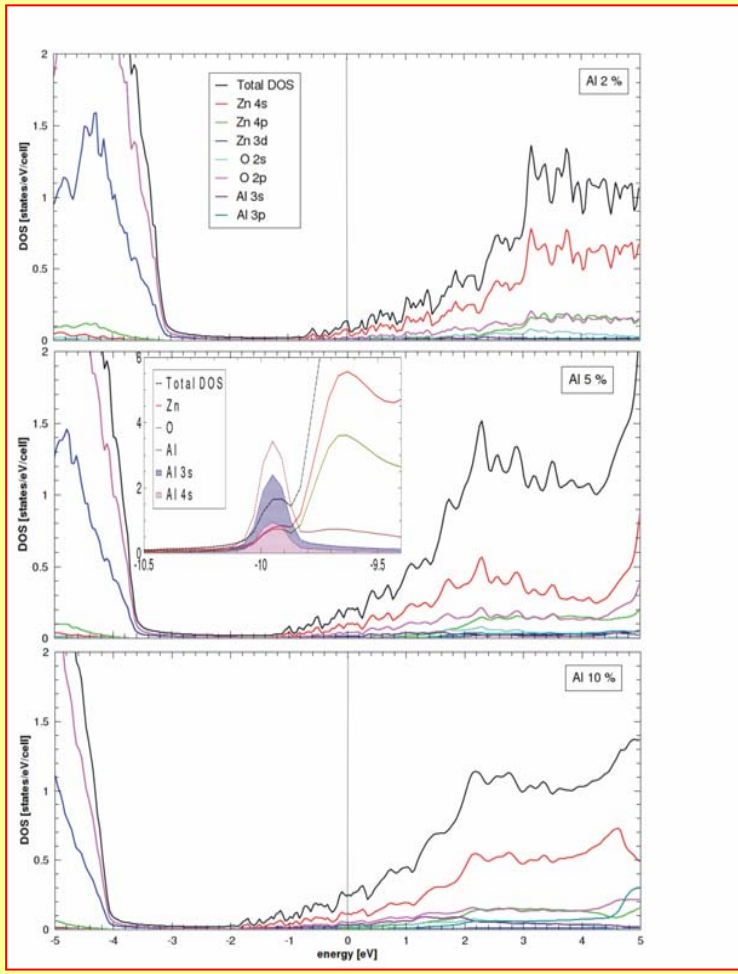
L(S)DA and LSDA+U, CPA-FPLO code [1].

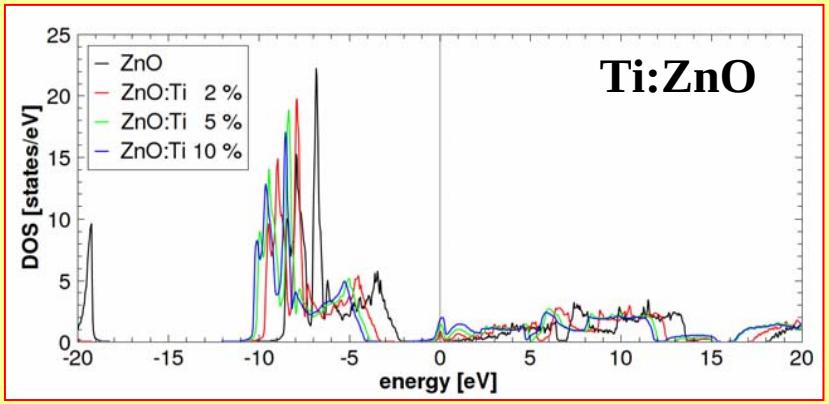
- wurtzite-type $Zn_{1-x}TM_xO$ (TM= Al, Ti, Mn) x= 2, 5 and 10 %
- substitutional disorder at Zn site.
- no lattice relaxation ==> only electronic effects.

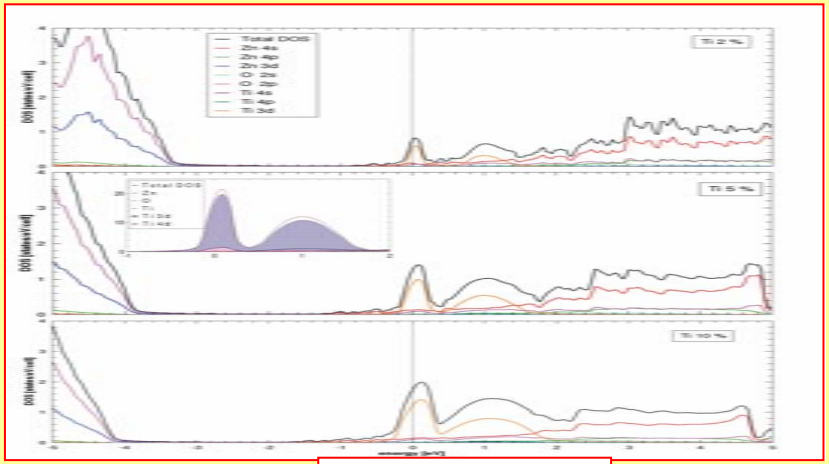


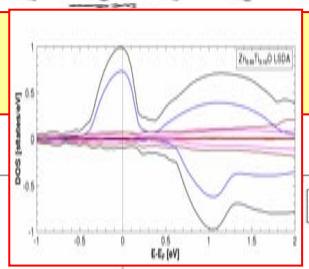
Al:ZnO



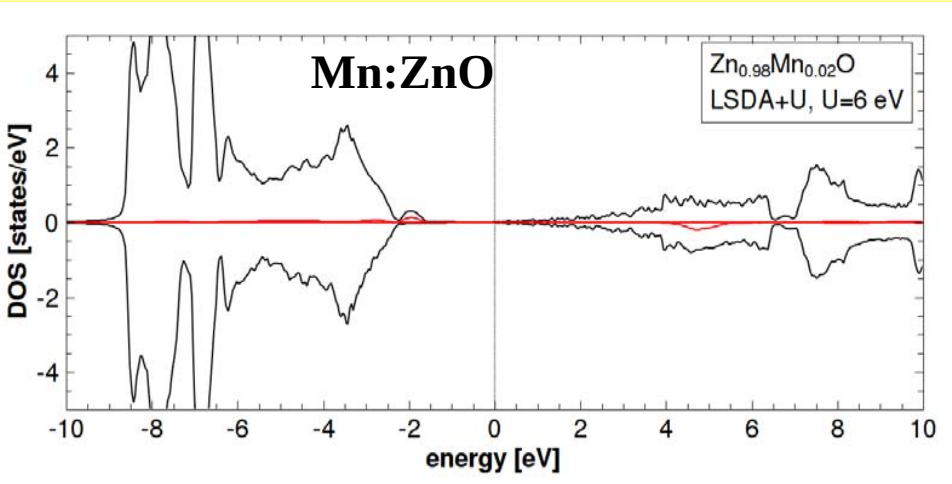


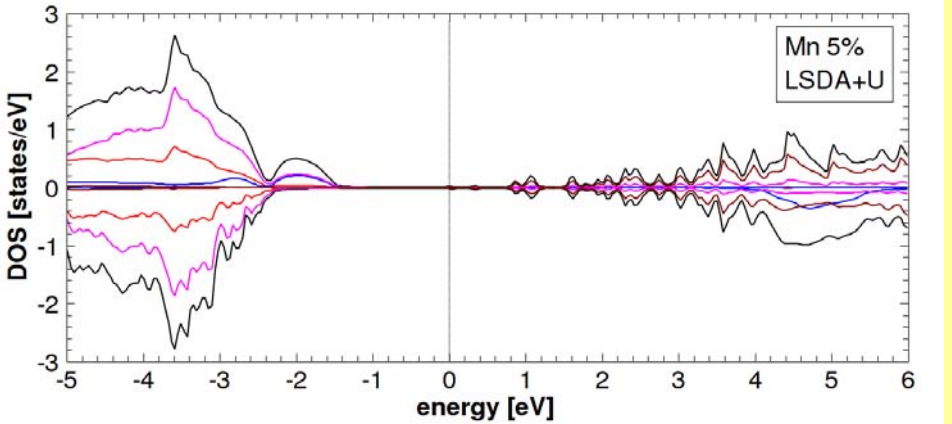

Ti:ZnO
ZnO
ZnO:Ti 2 %
ZnO:Ti 5 %
ZnO:Ti 10 %
DOS [states/eV]
energy [eV]





Total DOS
Zn 3d
Ti 3d
O 2p
Zn 4s
Zn0.90Ti0.10O LSDA
DOS [states/eV]
E-EF [eV]


Mn:ZnO
Zn0.98Mn0.02O
LSDA+U, U=6 eV
DOS [states/eV]
energy [eV]


Mn 5%
LSDA+U
DOS [states/eV]
energy [eV]

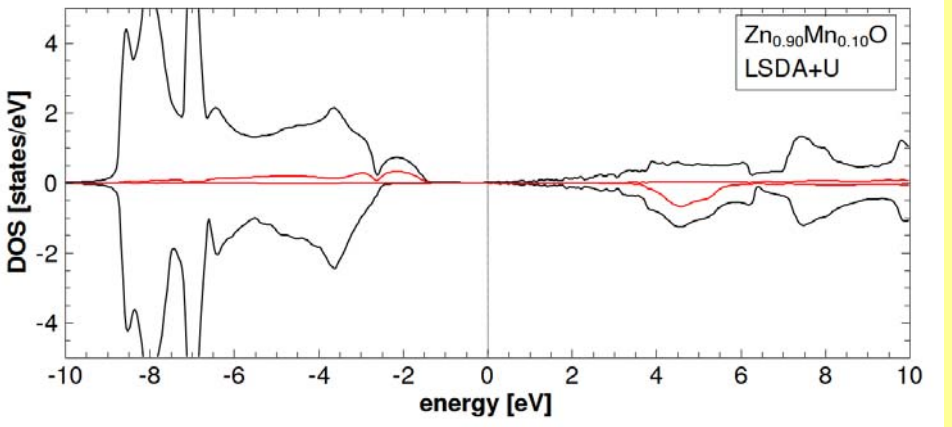
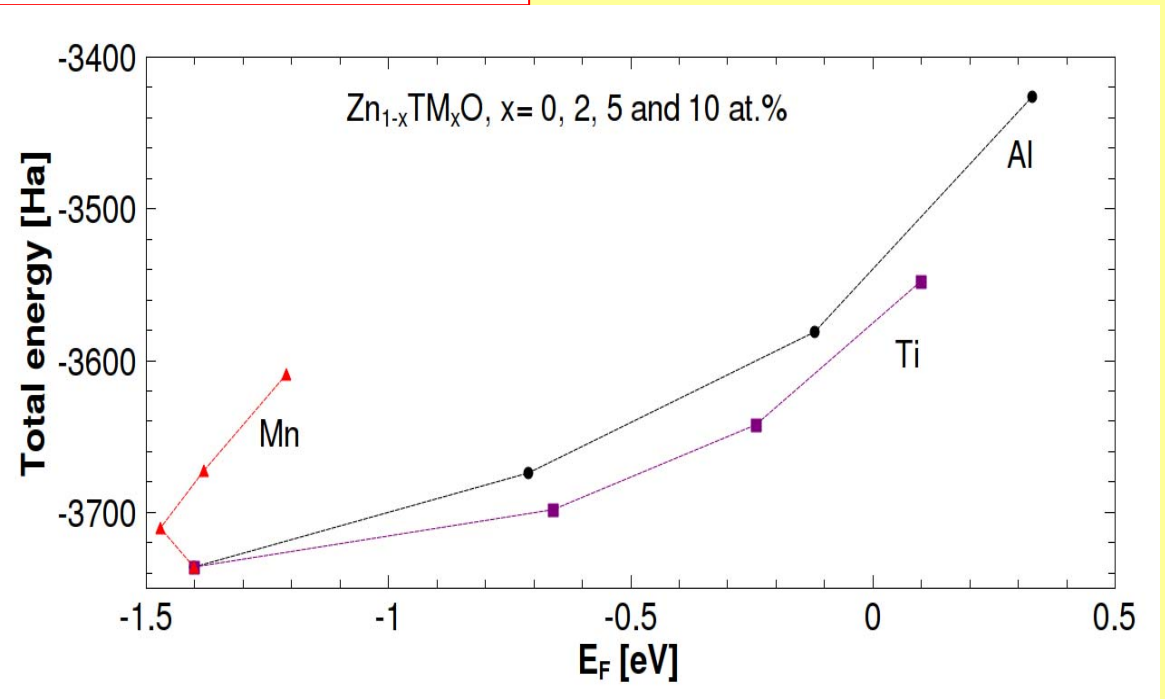

Zn0.90Mn0.10O
LSDA+U
DOS [states/eV]
energy [eV]

Table 1. Magnetic moment per 3d ion, m, and per formula unit, M, in Ti/Mn:ZnO.

x (3d)	(at.%)	2	5	10
m (μ_B/at)	Ti	0.90	1.13	1.28
	Mn	4.71	4.71	4.71
M (μ_B/f.u.)	Ti	0.02	0.06	0.13
	Mn	0.10	0.25	0.50



Conclusions

- **Al-doped ZnO multilayered films with hexagonal wurtzite structure were grown by sol-gel route on Si/SiO_2 and glass substrates.**

- **The substrate effect on films structure:**

a) Si/SiO2 substrate : nanostructured ZnO:0.5% at.Al layers (crystallites of 3-15 nm) with preferential (002) orientation;

b) Glass substrate : nanostructured ZnO:0.5at%Al (crystallites of 6-10 nm) randomly oriented.

- **Thickness of 10 layers : about 100 nm. The ZnO crystal structure could be observed starting with 4-5 layers deposition.**

- **The transmittance of the 1-10 layers of ZnO:0.5at%Al is in the range of 80%-90% in the visible and near infra-red regions.**

- **Fluorescence emission shows the presence of defects, interstitial Zn, OVs.**

- **The optical band edge of ZnO is shifted to a shorter wavelength when increasing Al concentration (blue shift). Optical transmittance spectra and Moss–Burstein theory..**

- **Ab-initio calculations predict : *i)* Al, Ti, Mn behave as donors; *ii)* different effects on conductivity and magnetism; *iii)* local magnetic moments in T and Mn:ZnO.**