EPR probing with Mn^{2+} ions of ZnO nanostructures

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Summary: The efficient tailoring of the material properties of doped nanostructures for specific applications involves knowledge and control of both structural aspects (size, morphology, crystallinity), as well as impurity content and distribution in the nanostructures. Such information was obtained by electron paramagnetic resonance (EPR) of low concentrations of Mn^{2+} ions in ZnO nanoparticles (NPs), synthesized by a variety of thermo–chemical procedures, and nanostructured ZnO thin films, deposited onto r-cut sapphire substrates by RF magnetron sputtering at room temperature.

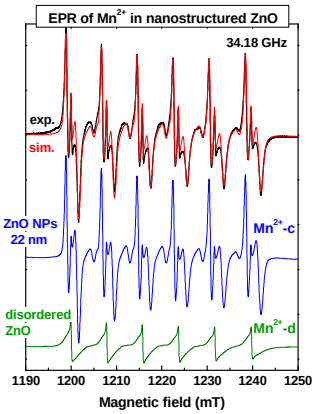
Using the weakly perturbing Mn^{2+} ions, localized substitutionally at Zn^{2+} sites in the host lattice, as paramagnetic probes, we have evidenced the dominance of size induced lattice disorder in ZnO NPs, independent of the synthesis procedures, and established an empirical relationship between the disorder induced EPR line broadening and the average crystallite size in ZnO NPs. Based on this relationship we have determined the growth mechanism of the ZnO NPs prepared by the thermal decomposition of hydrozincite.

We have also investigated the Mn^{2+} ions distribution in the as-deposited and thermally annealed nanostructured ZnO films and demonstrated a simple, statistically relevant and non-destructive procedure of quantitative determination of the paramagnetic impurities segregated at the grain boundaries (GBs) in nanostructured semiconducting and insulating films.

Samples:

- **ZnO NPs** prepared by thermal decomposition of precursors (hydrozincite (ZCB), $Zn(OH)_2$) or different liquid-liquid reactions (reactants, pH, *T* etc.)
- **ZnO thin film** deposited by RF - Magnetron Sputtering - UVN-75R1 (1.78 MHz) system at ~ 80 W in pure argon, on r-cut sapphire substrate at ~ 80°C

EPR: X (9.5 GHz)- and Q (34 GHz)-band Bruker ELEXSYS-E580X and -E500Q spectrometers (cetresav.infim.ro)
TEM / HRTEM: analytical high resolution JEOL ARM 200F electron microscope



- Line broadening effects due to strain / disorder induced fluctuations in the local crystal field included as Gaussian distributions of the axial *D* parameter

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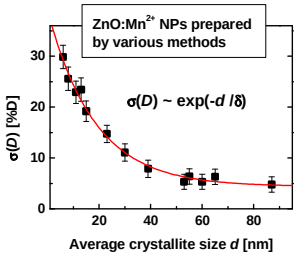
- Standard deviation = broadening parameter
  $\sigma(D) = 12\%\ D$
  $\sigma(D) = 43\%\ D$

S.V. Nistor, L.C. Nistor, M. Stefan, D. Ghica, Gh. Aldica, J.N. Barascu, *Cryst. Growth Des.* **11**, 5030 (2011)



- The degree of lattice disorder depends mainly on the ZnO NPs size
- ***Crystallite size determined by EPR!***

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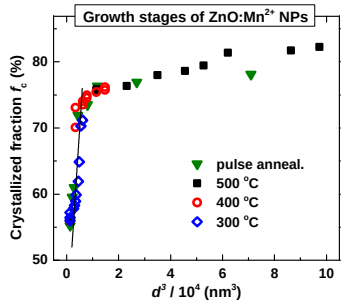
ZnO nanocrystallization process

ZCB sample annealed in air 240 °C / 90 min
→ ZnO NPs ~ 56% total ZnO
→ ZnO NPs: d_0 = 11 nm

- Isothermal annealing: 300 °C, 400 °C, 500 °C
- Pulse annealing: ΔT = 25 °C / 15 min
- Disordered and nanocrystalline (f_c) ZnO fractions measured from the double integration of Mn^{2+}-d and Mn^{2+}-c spectra

$$f_C(T,t) = \frac{X_C(T,t)}{X_C(T,t) + X_D(T,t)} \cdot 100\%$$



Two growth stages:

I. Free growth up to f_c ~ 75% , T < 400 °C – structural relaxation = local ordering by rearrangement of the atoms at interfaces
E_a = 23 kJ/mol
*** Reduction of surface induced strain ***
Narrower distribution of NPs size in this growth regime!

II. Larger crystallites grow at the expense of the smaller ones.
For T > 400 °C GBs diffusion becomes active, E_a = 79 kJ/mol
*** Reduction of the total grain boundary area ***

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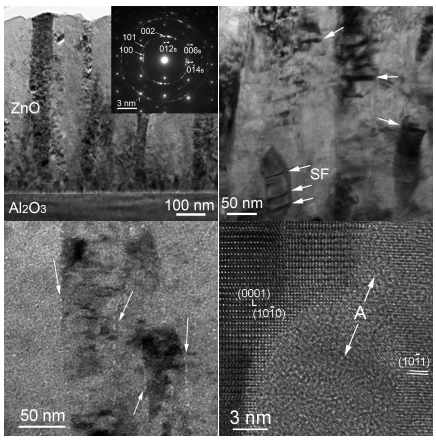
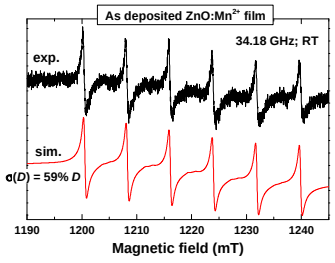
As-deposited ZnO film:

- Highly textured ZnO film of 580 nm thickness

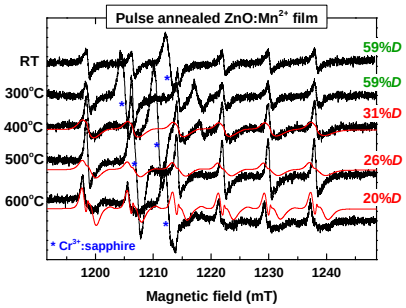
TEM / HRTEM:

- Coherence domains along [001] delimited by stacking faults (SF)
- Imperfect contact between the ZnO crystal grains, with rows of nanometric pockets trapped at the interfaces, filled with amorphous phase (A)





EPR: Only Mn^{2+}-d → all native Mn^{2+} localized in amorphous nano-pockets at the GBs



EPR: Mn^{2+}-c grows for T > 400 °C → crystallization of the amorphous phase + GBs diffusion

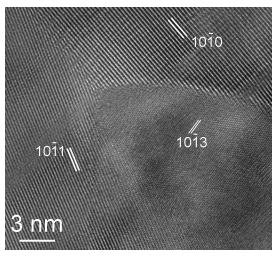
Pulse annealed ZnO film after annealing at 600 °C:

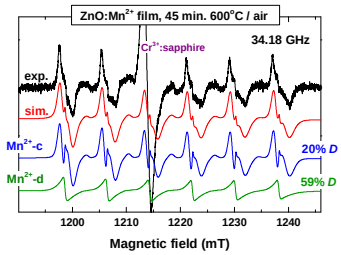
HRTEM:

- Well crystallized interfaces of the ZnO columns, with no amorphous inclusions

Quantitative EPR of Mn^{2+} ions:

- 37 % of the Mn^{2+} ions remain at the GBs (Mn^{2+} -d) while the rest – 63 % (Mn^{2+} -c) - are localized in the peripheral atomic layers of the ZnO columns, close to the GBs





- ***Simple, statistically relevant and non-destructive procedure to evaluate the amount of paramagnetic impurities segregated at the GBs in a nanostructured film***
- ***Can be used to determine the preparation conditions for doped nanostructured films with a required impurities distribution for envisaged applications***

D. Ghica, M. Stefan, C. Ghica, G.E. Stan, *ACS Appl. Mater. Interfaces*, under review

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