SPANISH - JAPANESE BILATERAL WORKSHOP

GOBIERNO DE ESPAÑA MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

SJ-NANO 2013 JST

"NANOTECHNOLOGIES AND NEW MATERIALS FOR ENVIRONMENTAL CHALLENGES"

TSUKUBA (JAPAN) March 5th, 2013

Epochal Tsukuba International Congress Center, Tsukuba, JAPAN

UV-VIS OPTOELECTRONICS WITH OXIDES

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ELECTRONICS ENGINEERING DEPT.

UNIVERSIDAD POLITECNICA DE MADRID (UPM), MADRID, SPAIN

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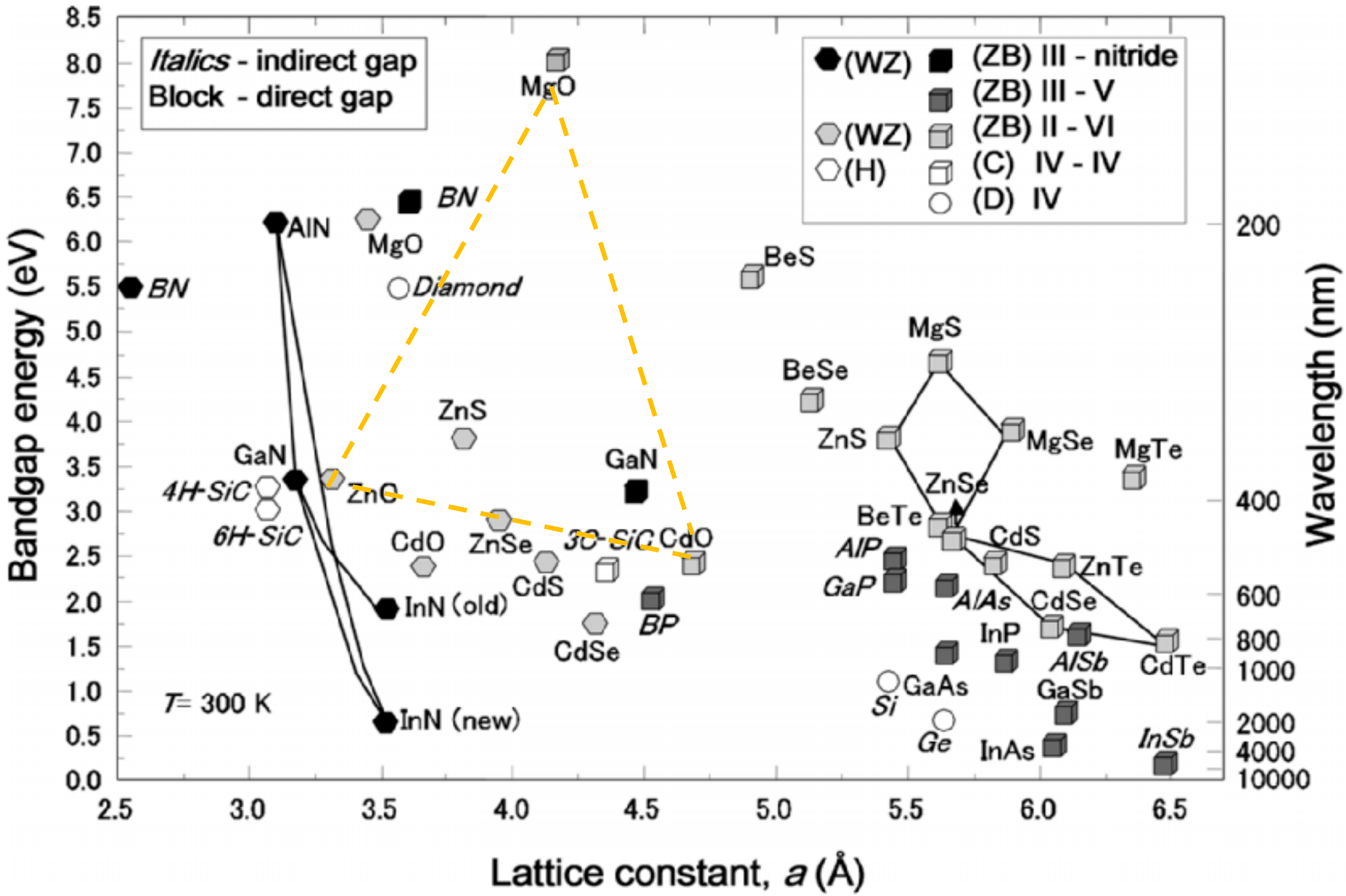
Research Institute of Electronics, Shizuoka University, Hamamatsu

JOINT JST-MINECO PROJECT, SU-UPM collaboration

Zn(Mg,Cd)O NANOSTRUCTURES FOR OPTOELECTRONICS



From "Wide bandgap semiconductors", Springer 2007.
K. Takahashi, A. Yoshikawa, A. Sandhu, editors.

162 Committee JSPS

Why ZnCdMgO?

ZnO

- ❖ Easy to grow with with different plane orientations
- ❖ High exciton binding energy ~60 meV; Excitonic effects at RT
- ❖ ZnO high quality substrates already available for homoepitaxy
- ❖ A variety of nanostructures/shapes easily grown
- ❖ Reactive surfaces and prone to get –OH groups

ZnCdO → ZnO → $Zn_{1-x}Mg_xO$

- ❖ Potentially , bandgap control from (VIS) ~ 2.2 eV to (UV) ~ 8 eV
- ❖ As an example, from present work, ZnMgO keep WZ structure up to ~Mg 50% (4.4 eV)

DIFFICULTIES

-to reach high Mg/Cd m fractions while keeping WZ S (NPS)

-to obtain reliable and robust p-type doping

-CAN ZnCdMgO NANOSTRUCTURES HELP TO CIRCUNVENT SUCH PROBLEMS?

Doping Asymmetry Problem in ZnO: Current Status and Outlook

In pursuit of improved optoelectronic devices, current experimental efforts to achieve p-type ZnO are examined along with techniques for testing GaN and ZnO doped with magnetic ions.

By VITALIY AVRUTIN, *Member IEEE*, DONALD J. SILVERSMITH, *Life Senior Member IEEE*, AND HADIS MORKOÇ

Vol. 98, No. 7, July 2010 | PROCEEDINGS OF THE IEEE 1269

PRL **108,** 215501 (2012) PHYSICAL REVIEW LETTERS week ending 25 MAY 2012

p-Type Conductivity in N-Doped ZnO: The Role of the N_{Zn}-V_O Complex

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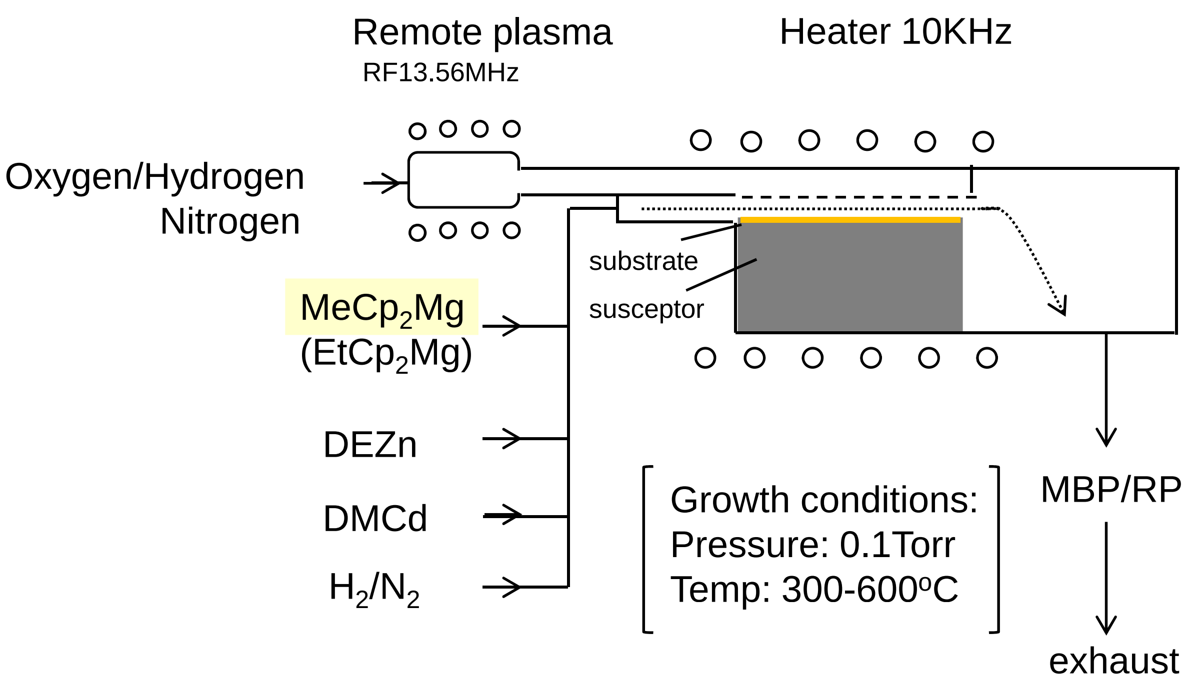
(Received 4 February 2012; published 23 May 2012)

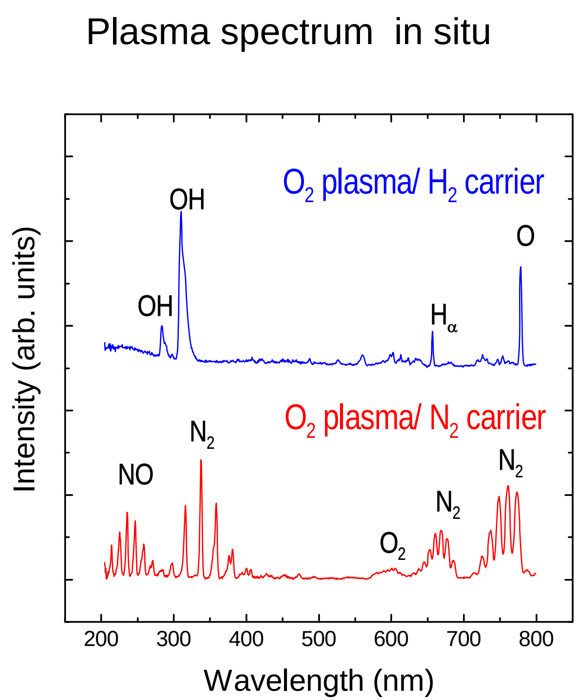
outline

- **RPE-MOCVD growth reactor at SU**
- **ZnCdO nanowires grown on a Sapphire paternned substrate: search for high Cd content**
- **Acceptors in undoped ZnMgO**
- **Typical p-doping results in ZnMgO layers**
- **Acceptors in N-doped ZnMgO**
- **MQW ZnCdO/p-type SiC green LED**
- **Summary/reflections**

Zn(Mg,Cd)O:N by RPE-MOCVD

A. Nakamura, J. Temmyo, Shizuoka U.





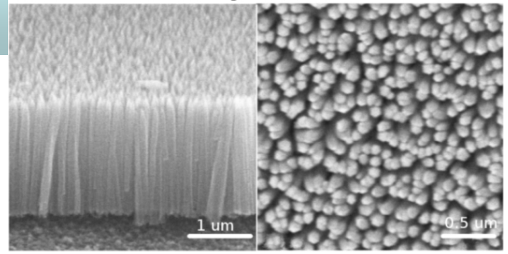
Highly non-equilibrium growth:

- radical energy enhances decomposition and doping
- WZ type ZnO alloys become available

STRUCTURAL and OPTICAL PROPERTIES of ZnCdO NANOCOLUMNS

- PL+HRXRD*+microEDX+HRTEM* of ZnCdO nanocolumns

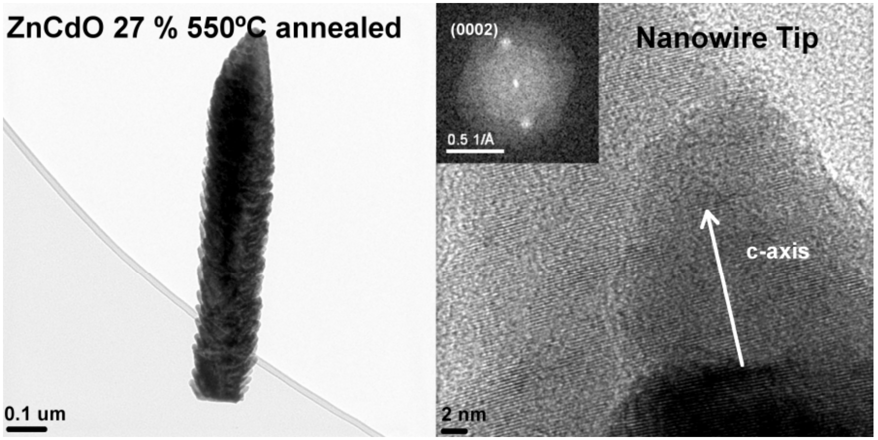
SEM

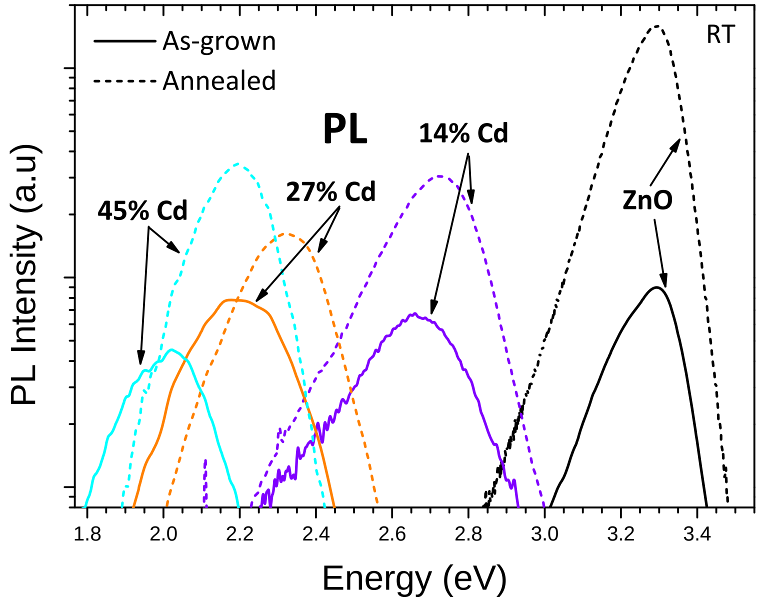


*HRTEM/EDX collaboration with V.Muñoz, U.Valencia, SP

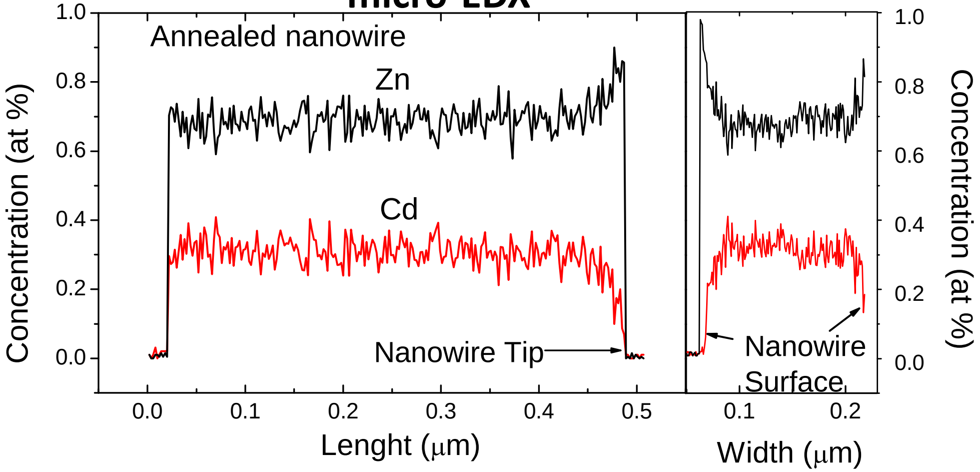
- **Cd%: x=0, 0.14, 0.27 and 0.45!!**
- Length → 1-4 μm
- Diameter → 100-200 nm

HRTEM





micro-EDX

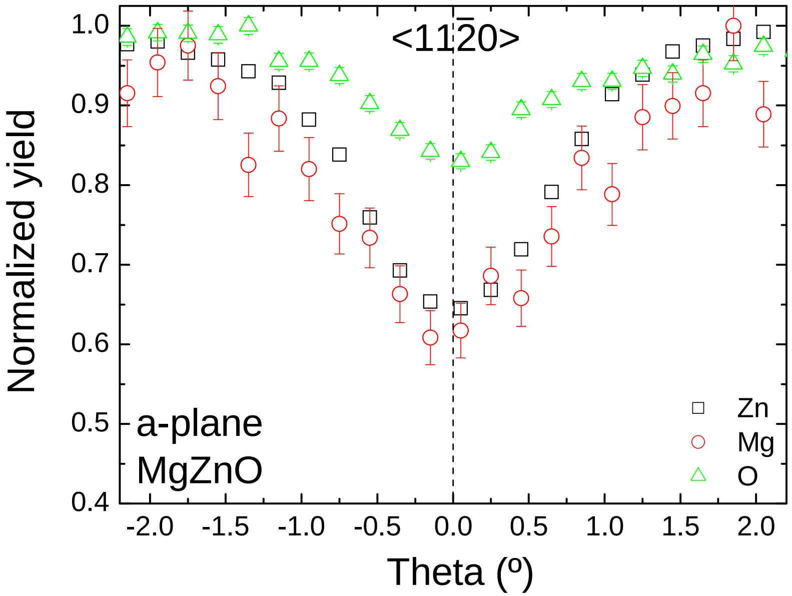


1. **Emission demonstrated down to 2.02 eV**
2. **Only wurtzite phase observed even for 45% Cd, no phase separation!**
3. **State of the art ZnCdO nanocolumns!**

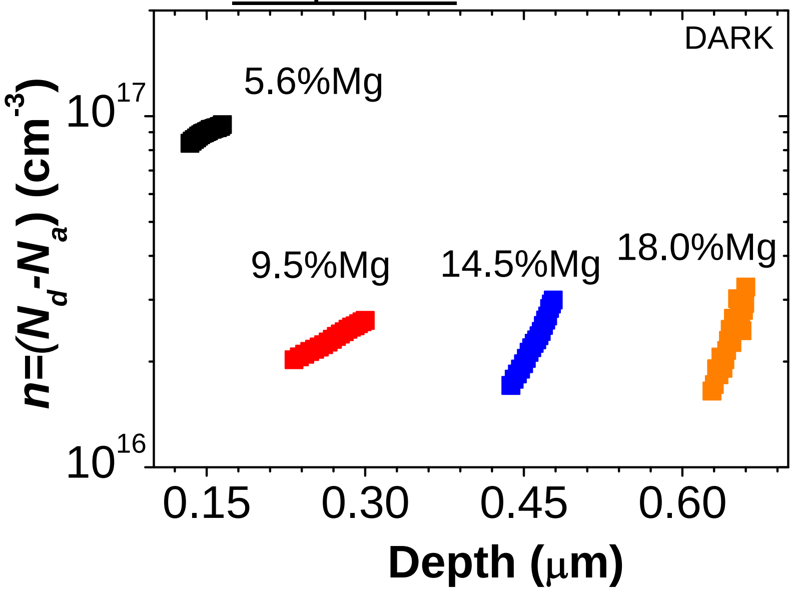
Results accepted for publication in Appl.Phys.Lett.

CHARACTERIZATION of ZnMgO (MOCVD) LAYERS (SU)

*RBS determination of stoichiometry and quality**



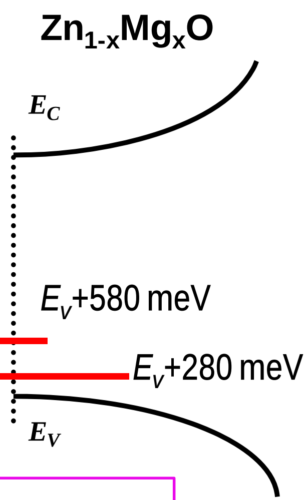
C-V profiles



*Collaboration with A. Redondo, ITN, Portugal

DLOS + Lighted CV profiling

Mg (%)	$n=(N_d-N_a)$ (cm^{-3})	E_v+280 meV (cm^{-3})	E_v+580 meV (cm^{-3})
5.6	8.02×10^{16}	1.08×10^{17}	1.66×10^{16}
9.5	1.98×10^{16}	3.44×10^{17}	1.54×10^{16}
14.5	1.47×10^{16}	8.62×10^{17}	2.27×10^{16}
18.0	1.27×10^{16}	1.01×10^{18}	5.23×10^{16}



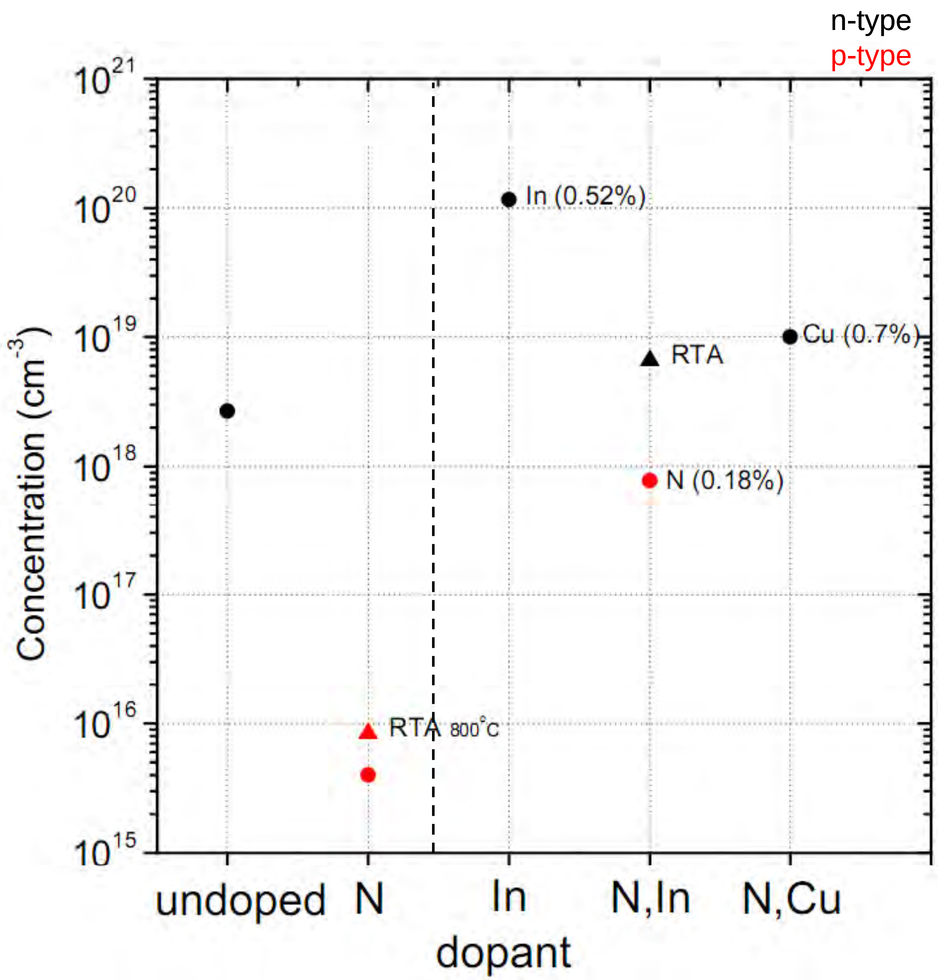
1. O-rich behavior of samples
2. Growth plane (a-plane or c-plane) does not affect Mg incorporation
3. ZnMgO is highly compensated due to two acceptor levels related to V_{Zn}
4. Can use ZnMgO samples to achieve p-type doping

Same V_{Zn} related acceptors also found in MBE ZnMgO layers from JM Chauveau, CNRS-CRHEA, FR

* A.F. Kohan et al. Phys.Rev.B 61, 15019 (2000)

Typical p-doping results

A. Nakamura, J. Temmyo, Shizuoka U.



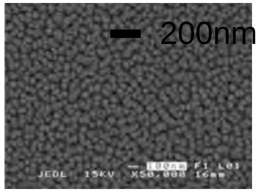
MgZnO:(N,In,Cu) co-doping showed p-type

- N solubility enhanced by codoping
- $(N)_O$ acceptor activated

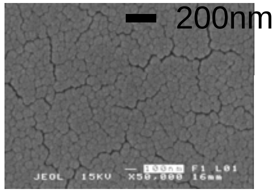
against expectation:

- n-type conductivity for N, Cu
- Conductivity-type change for N, In was occurred under RTA activation.

ref: morphology change after RTA



As grown

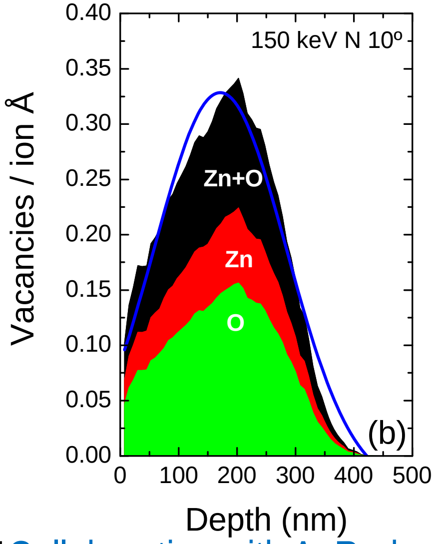


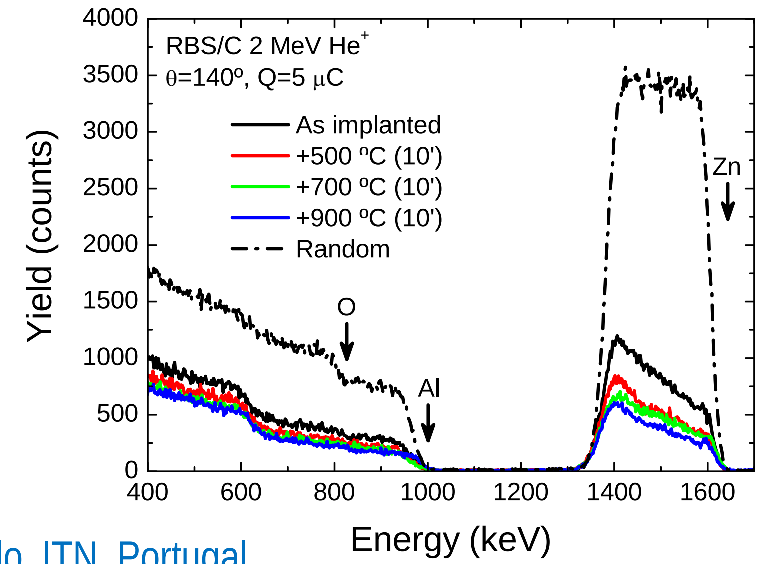
RTA 800°C

S. Mohanta, et al. J. Appl. Phys 110 (2011) 013524.

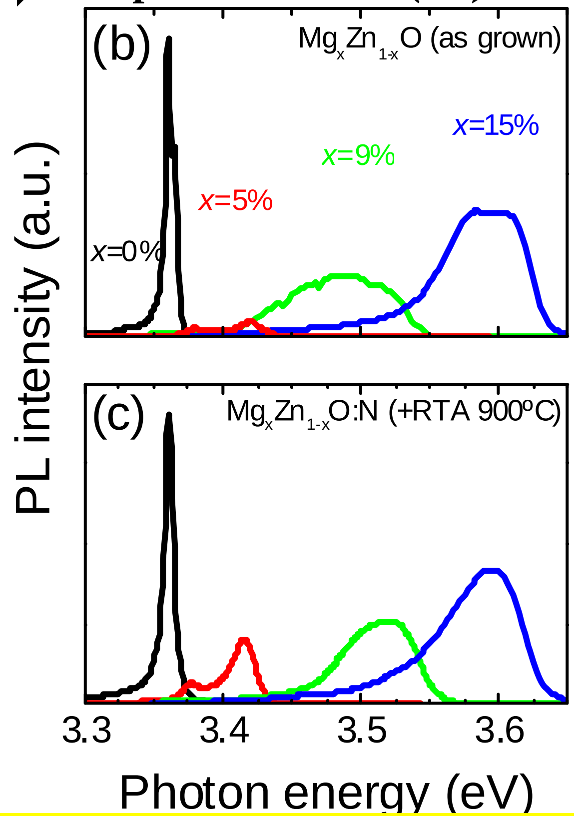
N-implantation in MOCVD ZnMgO LAYERS

**Implanted profile (SRIM)* ⟹ *Crystal recovery (RBS)* ⟹ *Optical emission (PL)*

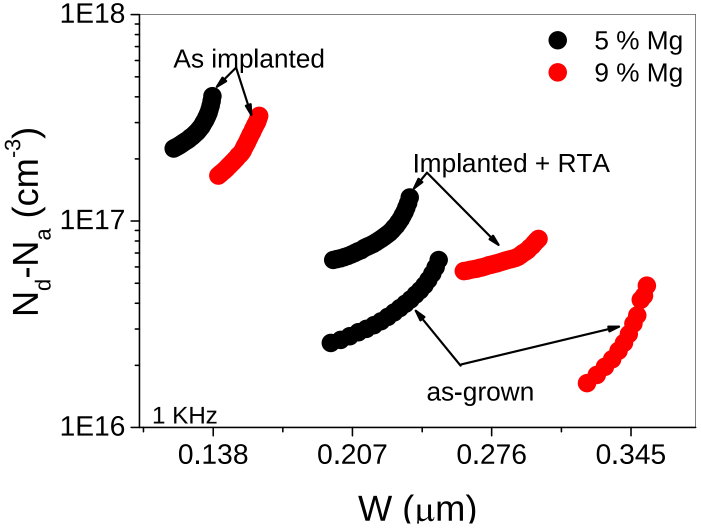




*Collaboration with A. Redondo, ITN, Portugal

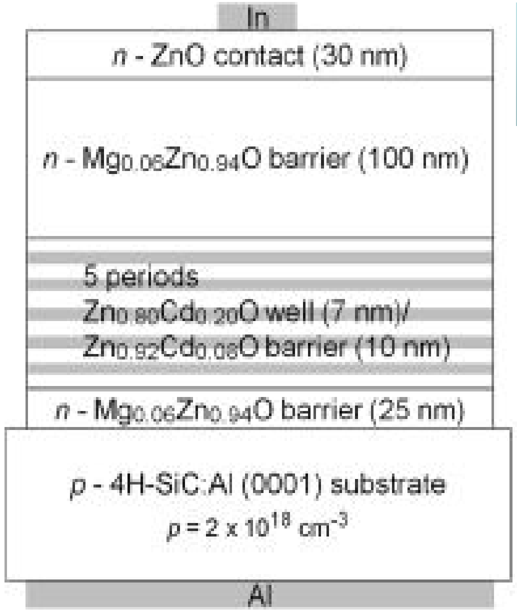


CV profiling using Schottky diodes

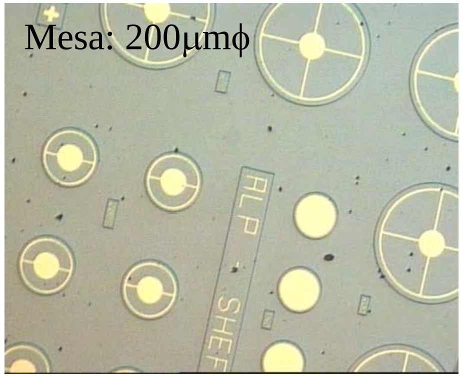


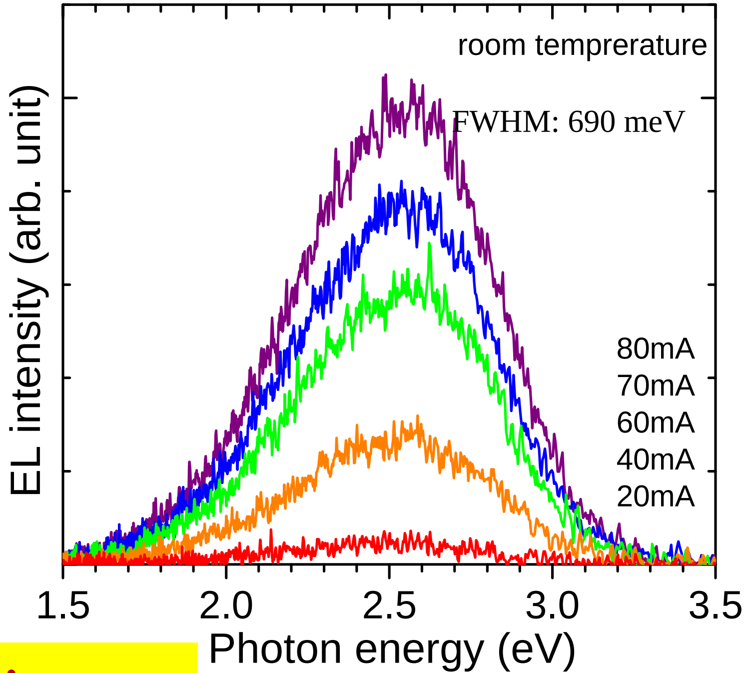
1. N implantation at 150 keV
2. Implanted films are highly n-type
3. Best crystal recovery found at 900°C (strong Al out-diffusion from substrate at higher T).
4. Thermal annealing reduces Xtal damage, films are less n-type, <u>BUT</u> no direct observation of p-type behavior ; defects overcome N-related acceptors

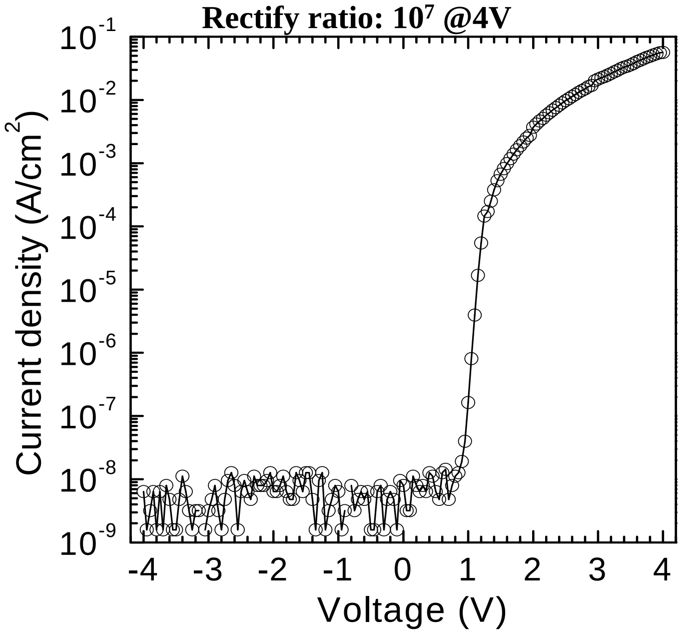
MQW ZnCdO/ZnO/p-SiC VIS LED



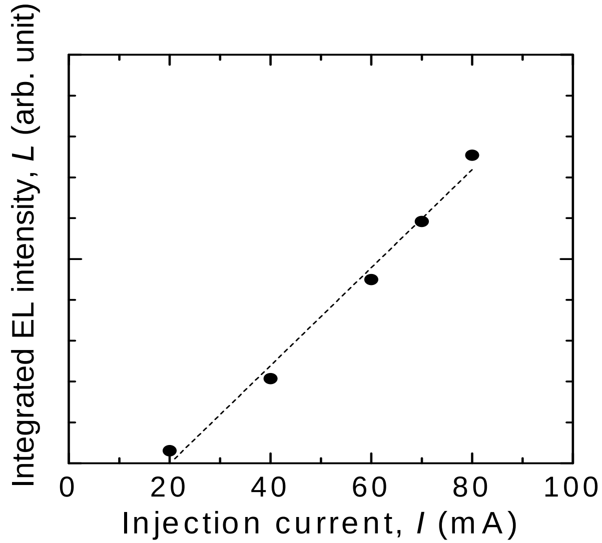
Layers grown at Shizuoka U.
5 QW ZnCdO (20% Cd)







1. RT CW Emission at 2.55eV (agreement with PL from ZnCdO/ZnO QW)
2. First demonstration of ZnCdO MQW LED in literature!!....green gap!



Results published in IEEE Photon.Tech.Lett.2011

SUMMARY

- **Single-phase wurtzite nanowires of ZnCdO, with Cd up to 50%, have been demonstrated by RPE- MOCVD (C-plane on sapphire)**
- **Single-phase wurtzite QW and thick layers of ZnMgO with Mg up to 55% have been demonstrated by MBE**

- **Both growth technologies grow quite far from equlibrium and Zinc vacancies are promoted**
- **Proper growth coditions and substrates seem to allow single phase WZ ZnMgCdO alloys for UV and VIS optoelectronics**

- **In N doped MgZnO alloys (MOCVD) and in N:ZnO (MBE) a shallow acceptor has been detected that seems to correspond to the N_O-V_{Zn} complex predicted by computer simulations and that may play a key role in obtaining robust p-type doping**

the future of ZnMgCdO alloys for optoelectronics still open….

Besides SU- UPM joint efforts, ….collaboration with other groups

1. Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications-CNRS (France)

Prof. Jean-Michel Chauveau

Samples grown by MBE: ZnMgO with very high Mg contents, and nonpolar ZnMgO/ZnO MQW structures; ZnO with low residual concentrations

-6 invited/oral presentations, -3 papers, -1 visit to UPM in 01/2013

2. Instituto Tecnológico e Nuclear (ITN, Portugal), Dr. Andres Redondo

Analysis of ZnMgO by RBS, N-implantation on ZnMgO; analysis of residual H in ZnO

-2 invited presentations, -2 papers

3. Ohio State University (EEUU), Prof. Steve Ringel

DLTS/DLOS, CV, analysis of ZnMgO and ZnO

-1 oral presentation, -1 paper, - OSU-UPM Agreement on research ongoing

-Visits to UPM in 10/2011 and 05/2012

4. Univ. Valencia (Spain), Prof. Vicente Muñoz-Sanjose

HRTEM and micro-EDX of ZnCdO, and ZnMgO samples grown by spray-pyrolisis

-1 oral presentation, -2 papers

-1 Joined MINECO-funded project (TEC2011-28076-C02-01)

5. University of Montpellier II (France), Prof. Pierre Lefebvre

Time resolved micro-photoluminescence, student exchange