4th International Symposium on Energy Challenges & Mechanics - working on small scales

11-13 August 2015
Aberdeen, Scotland, UK

Plenary Talk on Energy Harvesting using ZnO-Based Thin Films & Nanostructures

nanovation

D. J. Rogers, F. H. Teherani, P. Bove & V. E. Sandana — www.nanovation.com
M. Razeghi, CQD, Northwestern University — cqd.eecs.northwestern.edu

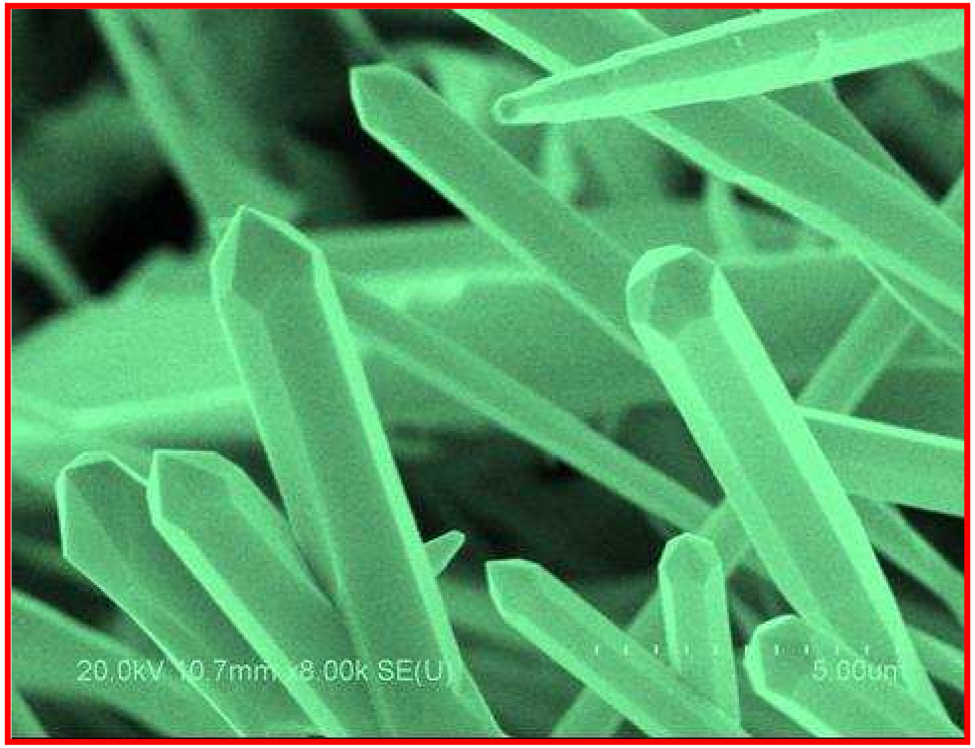
OUTLINE

nanovation

1. Background

2. Nanovation

3. Energy Harvesting
   - *Solar*
   - *Piezogenerators*
   - *Thermoelectrics*



Sandana, Rogers et al. J. Vac. Sci. Technol. B 27, 3 (2009) 1678

4. Conclusions

1. Background

Comparison of Wide Bandgap Materials

Material	Crystal Structure	Lattice constants a (Å)	c(Å)	Band gap at RT (eV)	Cohesive energy (eV)	Melting point (K)	Exciton binding energy (meV)
ZnO	Wurtzite	3.249	5.207	3.37	1.89	2248	60
GaN	Wurtzite	3.189	5.185	3.39	2.24	1973	21

ZnO vs GaN: Significant Differences

Exciton Binding Energy Higher for ZnO

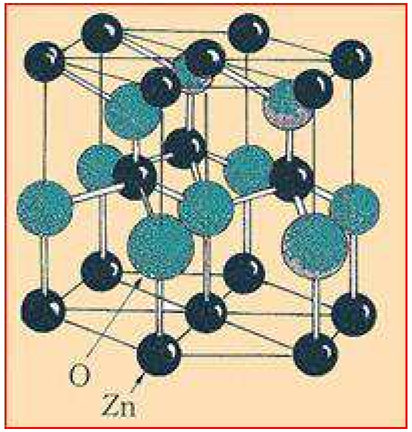
Wet etching possible for ZnO but not for GaN

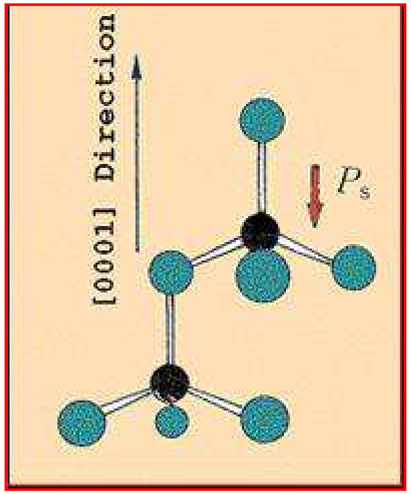
Availability of p-type GaN

Rogers et al.: Proc. SPIE 7605 (2010) 76050K-1

Other Interesting ZnO Properties…

Property	Specification	Comments
Piezoelectricity (e_{33})	1.2 C/m^2	among highest for all semiconductors
Transparency	85-95% in visible range	higher if doped with F or Ga
Electrical Resistivity	tuneable	semi-insulating ➔ semi-metallic
Wide Bandgap	tuneable	emits & detects UV light
Material Availability	no shortage	unlike Ga & In which are rare
Cost	very low	





www.hokudai.ac.jp

Biocompatibility of ZnO

U.S. Food and Drug Administration

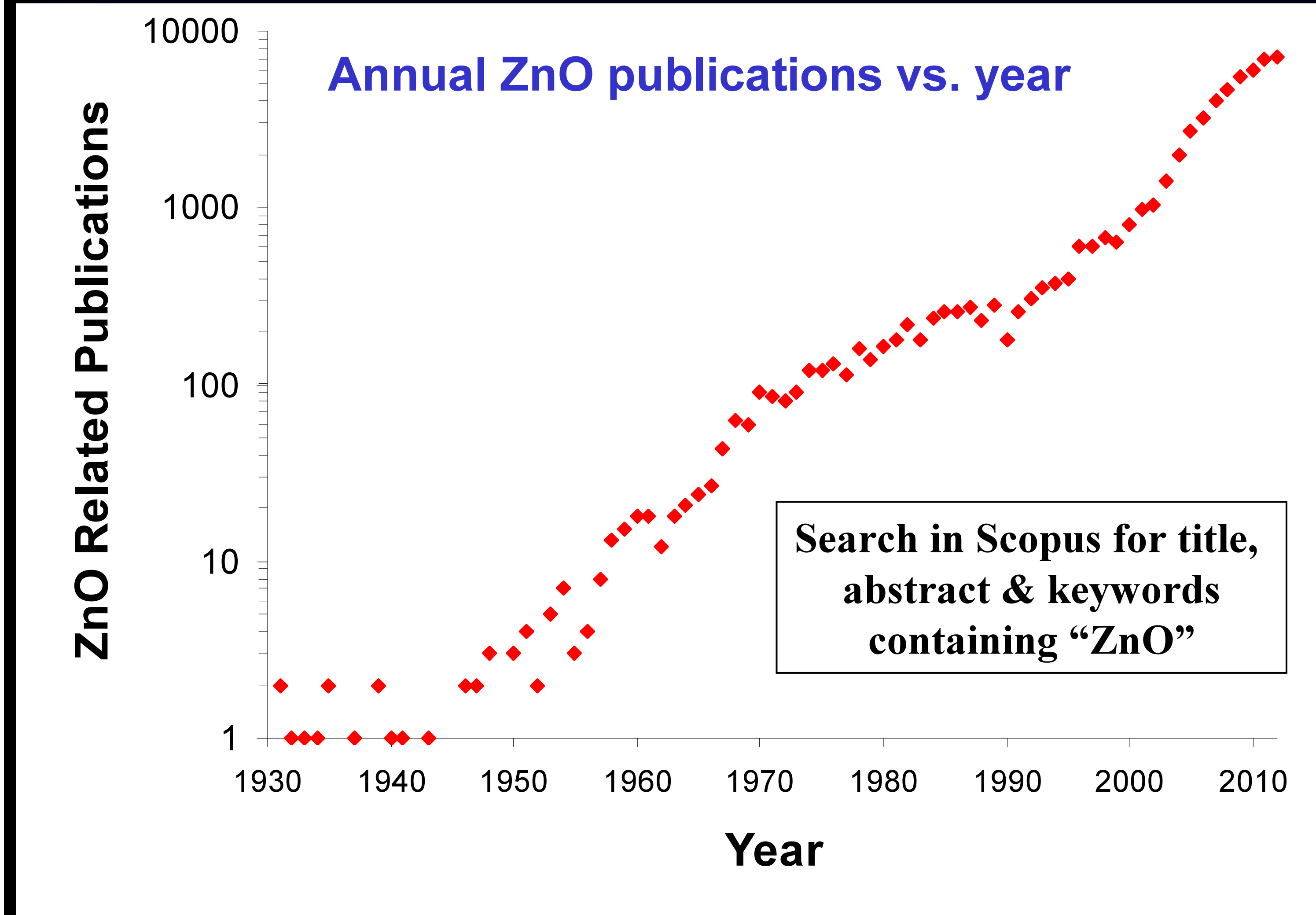
FDA

"GRAS" (generally regarded as safe) label.

ZnO in various pharmaceutical products & some vitamin pills…

Exponential increase in ZnO research

nanovation



2014 Publications

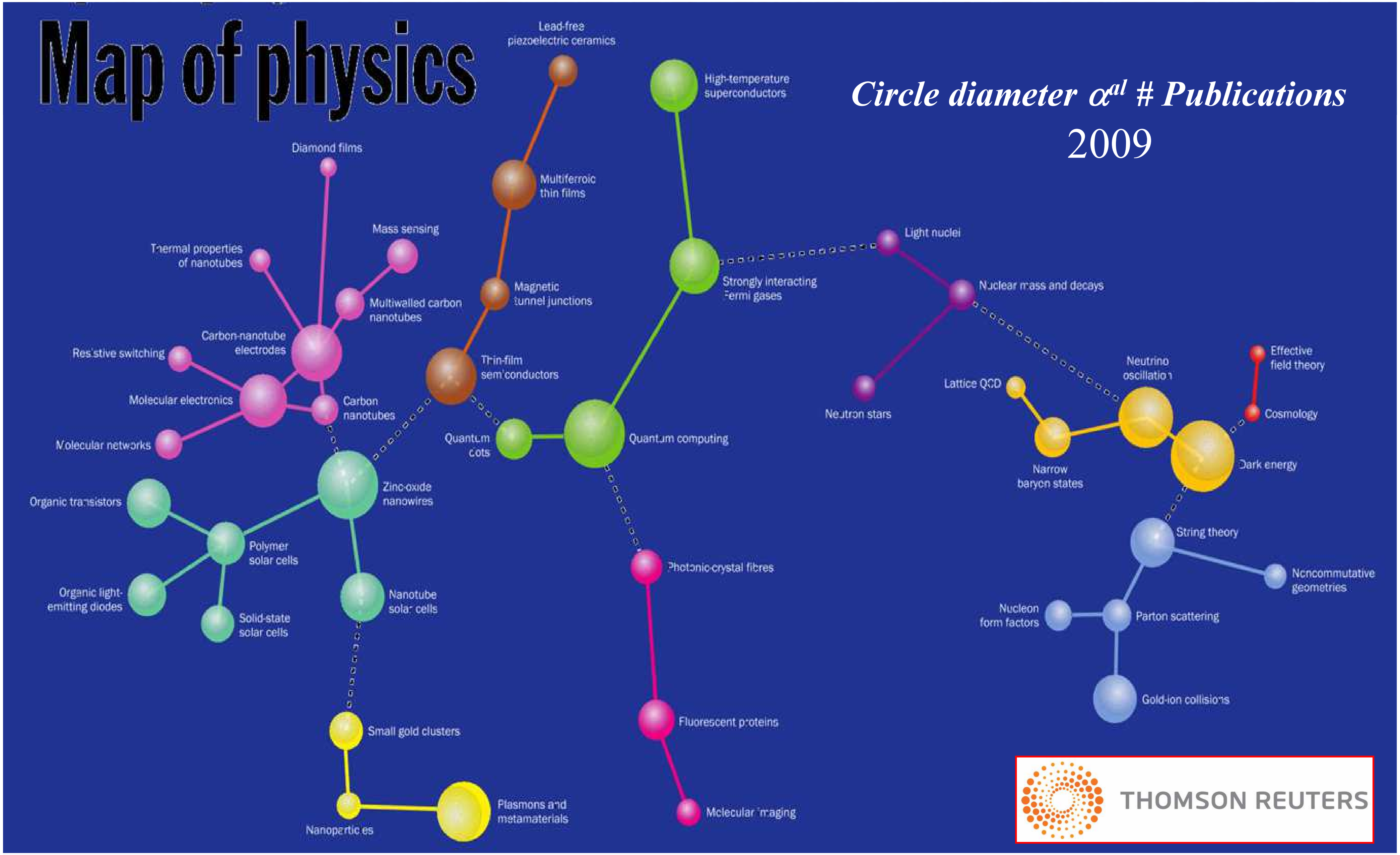
ZnO: 8035

GaN: 3502

Rogers et al. Laser Focus World 49, 10 October (2013)

Breakthroughs........

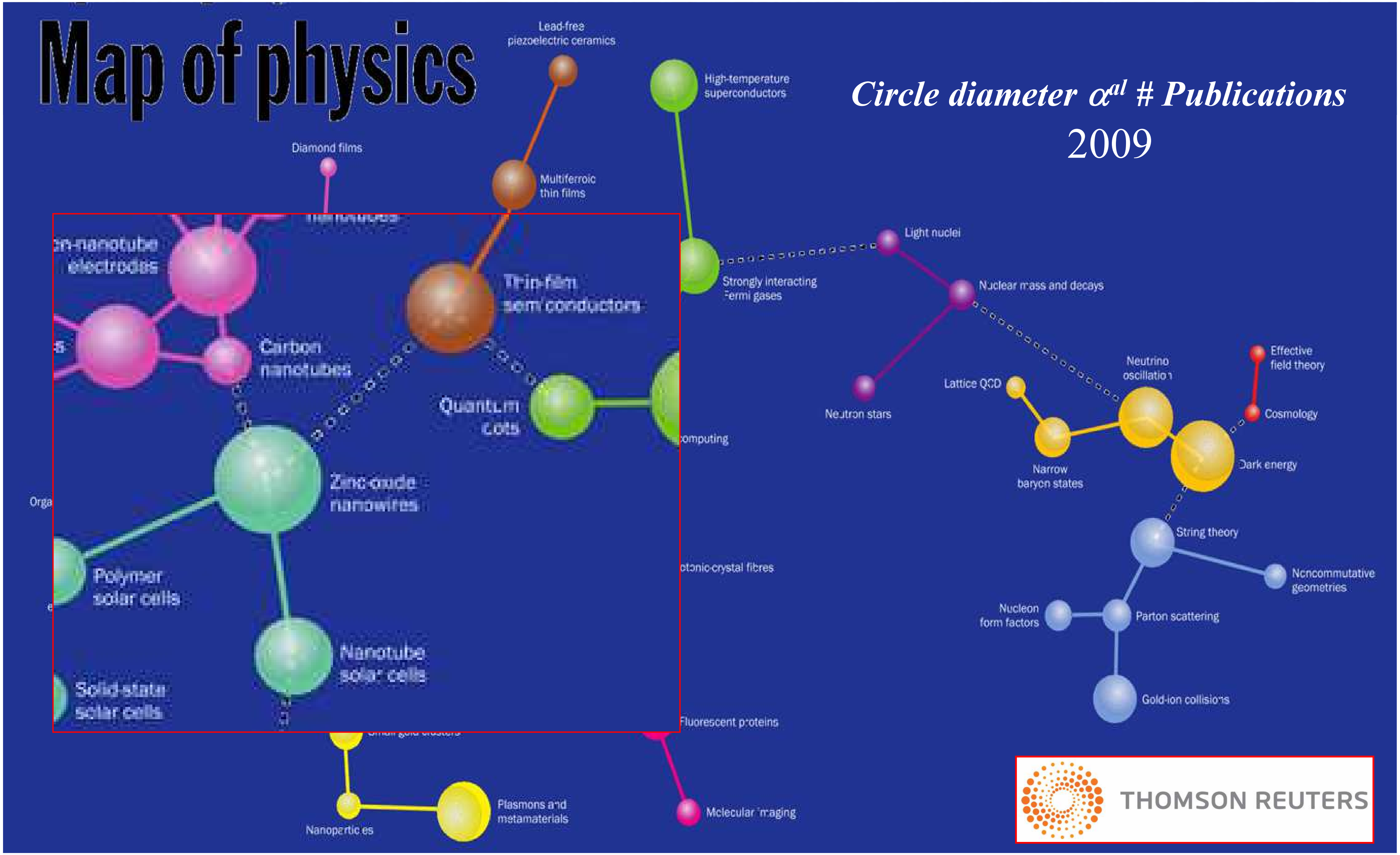
Rogers et al.: Proc. SPIE 7605 (2010) 76050K-1



nanovation

Energy Challenges & Mechanics
- working on small scales

Aug. 2015



Circle diameter α^{al} # Publications

2009

nanovation

Energy Challenges & Mechanics
- working on small scales

Aug. 2015

ZnO-Based Electronics Market

nanovation

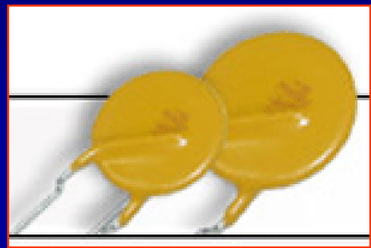
Energy Challenges & Mechanics
- working on small scales

Aug. 2015

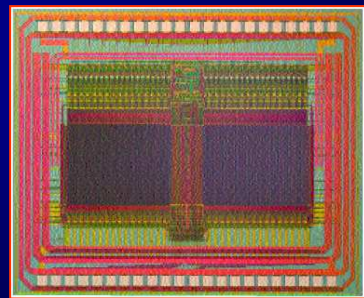
Established ZnO Thin Film Applications

Conductive & Optical Coatings

Gas sensors



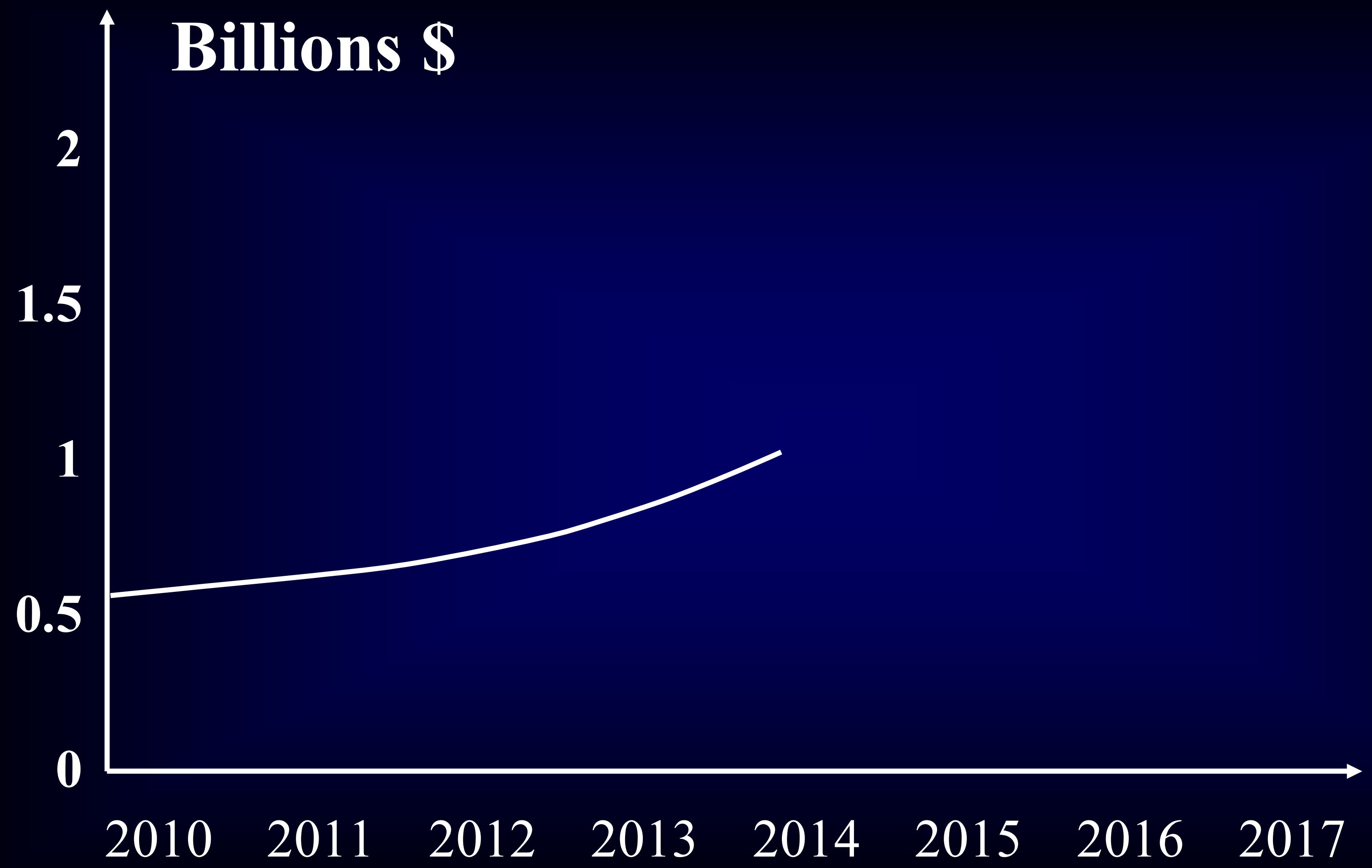
Surface Acoustic Wave devices



Varistors

New ZnO Electronics Market Forecast

nanovation



NanoMarkets

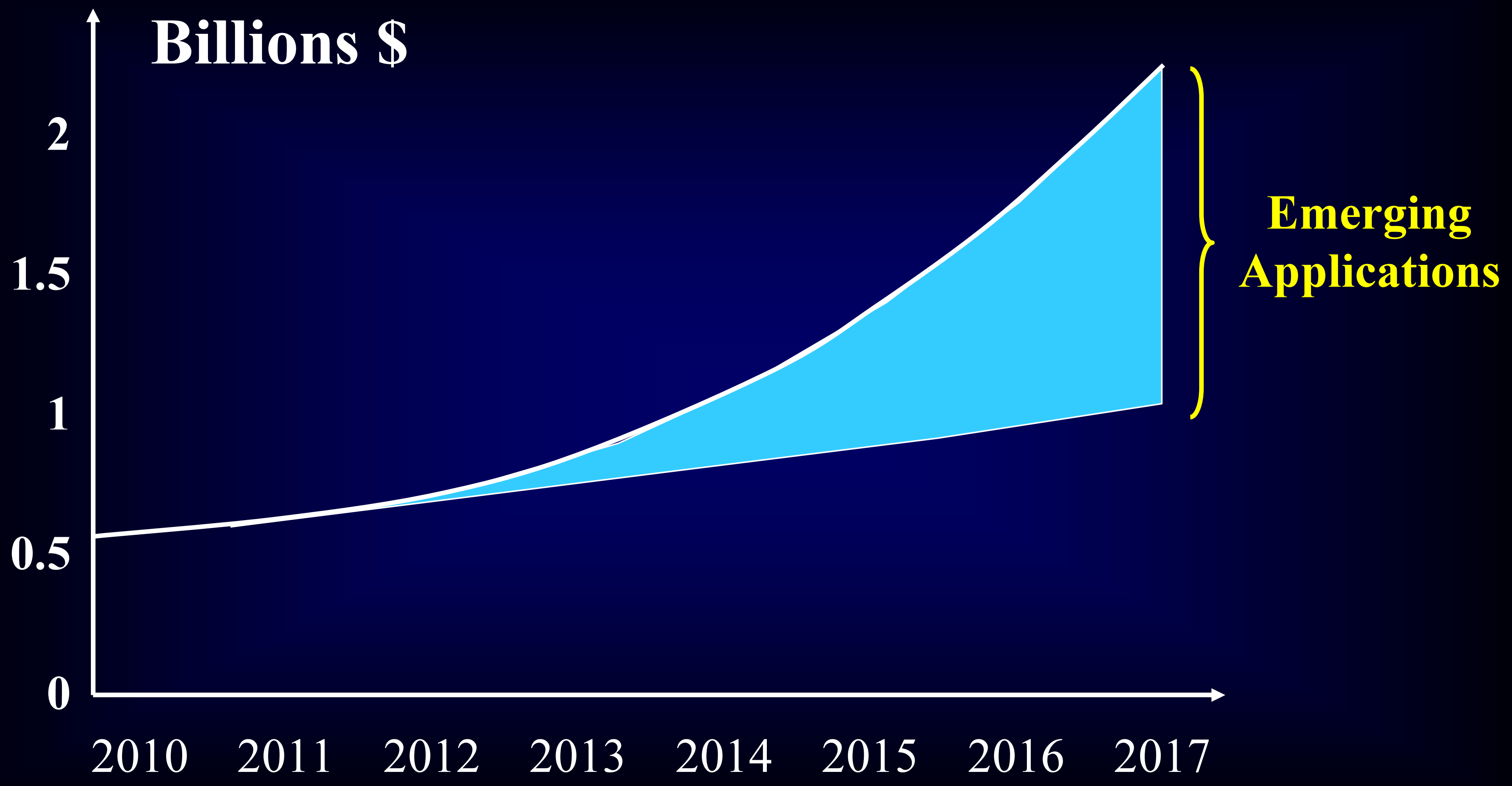
nanovation

Energy Challenges & Mechanics
- working on small scales

Aug. 2015

New ZnO Electronics Market Forecast

nanovation



NanoMarkets

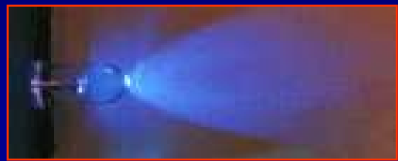
Aug. 2015

nanovation

Energy Challenges & Mechanics
- working on small scales

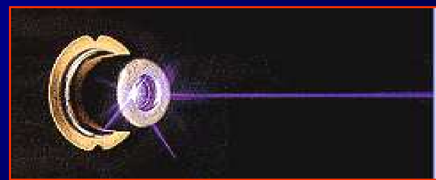
Nanomarkets Envisage 4 Key Emerging Applications

Photovoltaics



Displays

Light-Emitting Diodes (LEDs)



Sensors (Gas, UV & Bio)

NanoMarkets

« The leading players in this space at the present time are Canon, Casio, Cermet, Idemitsu, LG Electronics, ***Nanovation***, Samsung, Sharp, Tokyo Denpa, Toppan Printing, ZnOrdic & ZN Technology. »

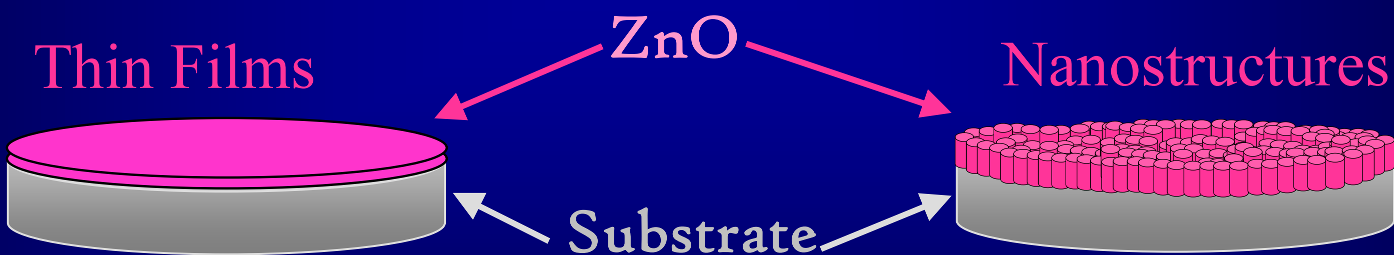
2. Nanovation

French ZnO
Start-up

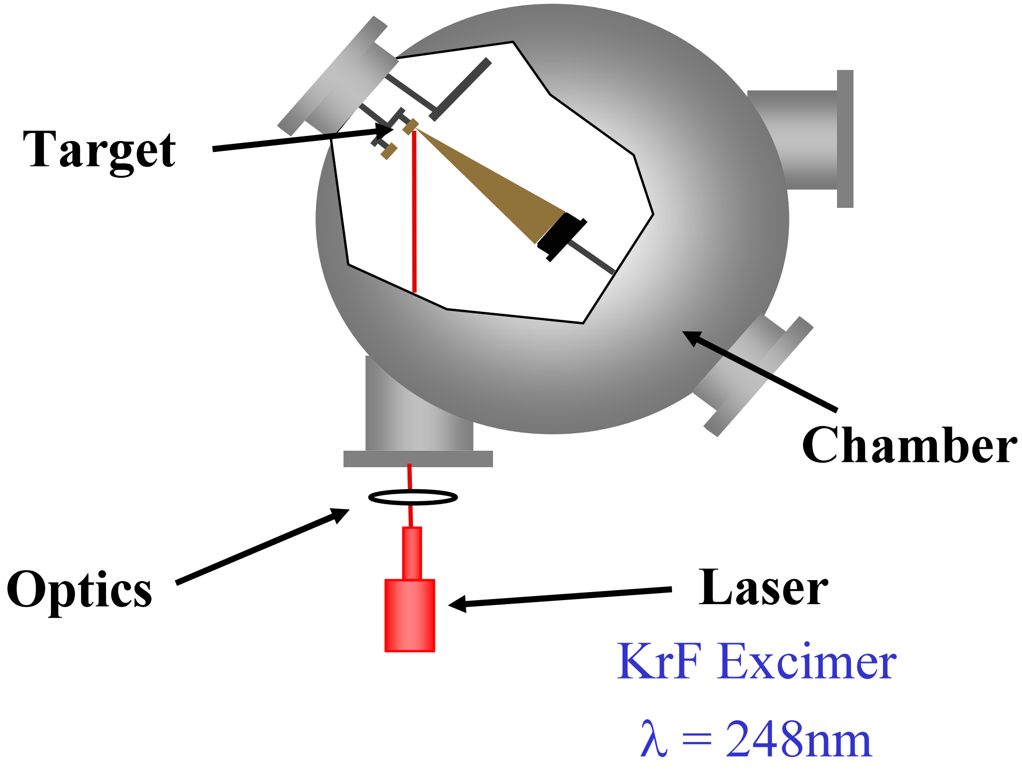
Founded 2001

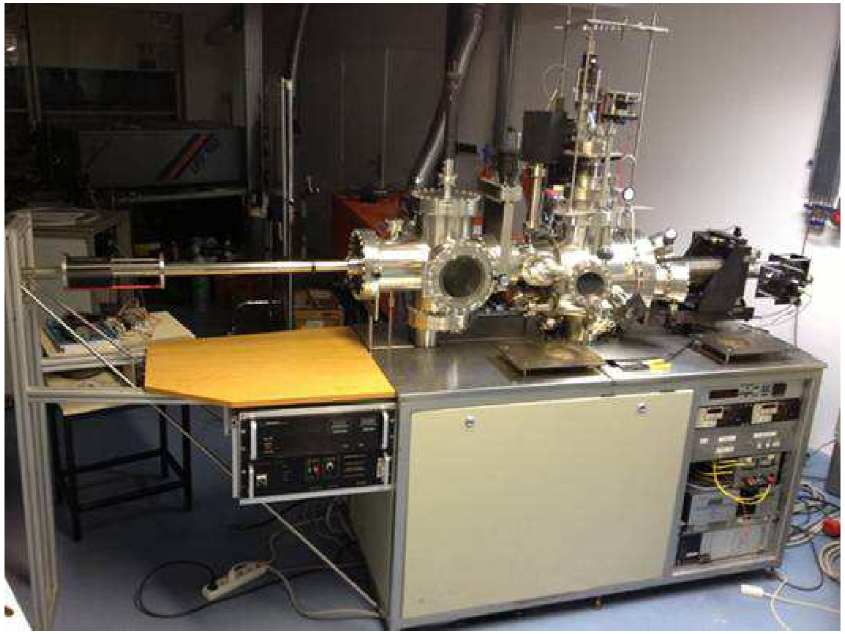
2011:
New Premises:
Châteaufort
(Saclay)

Product: Optoelectronic Grade ZnO Epiwafers

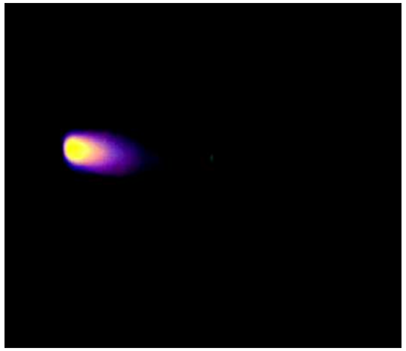
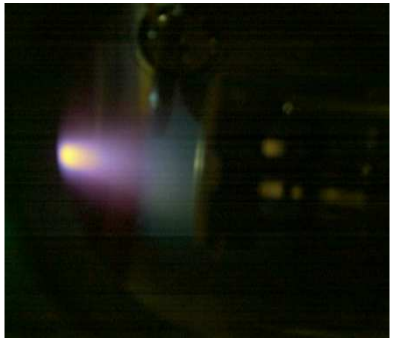
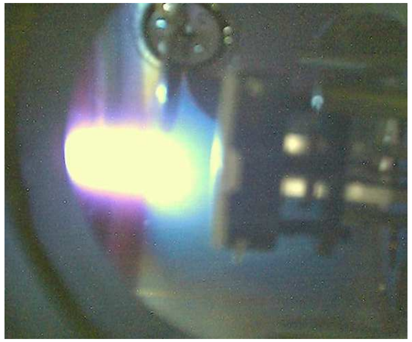
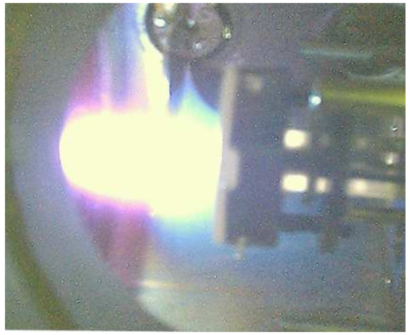


Production: Pulsed Laser Deposition (PLD)





Why is PLD so Good for Oxides?

PLD Impinging Species Kinetic Energy can be : 10-100eV

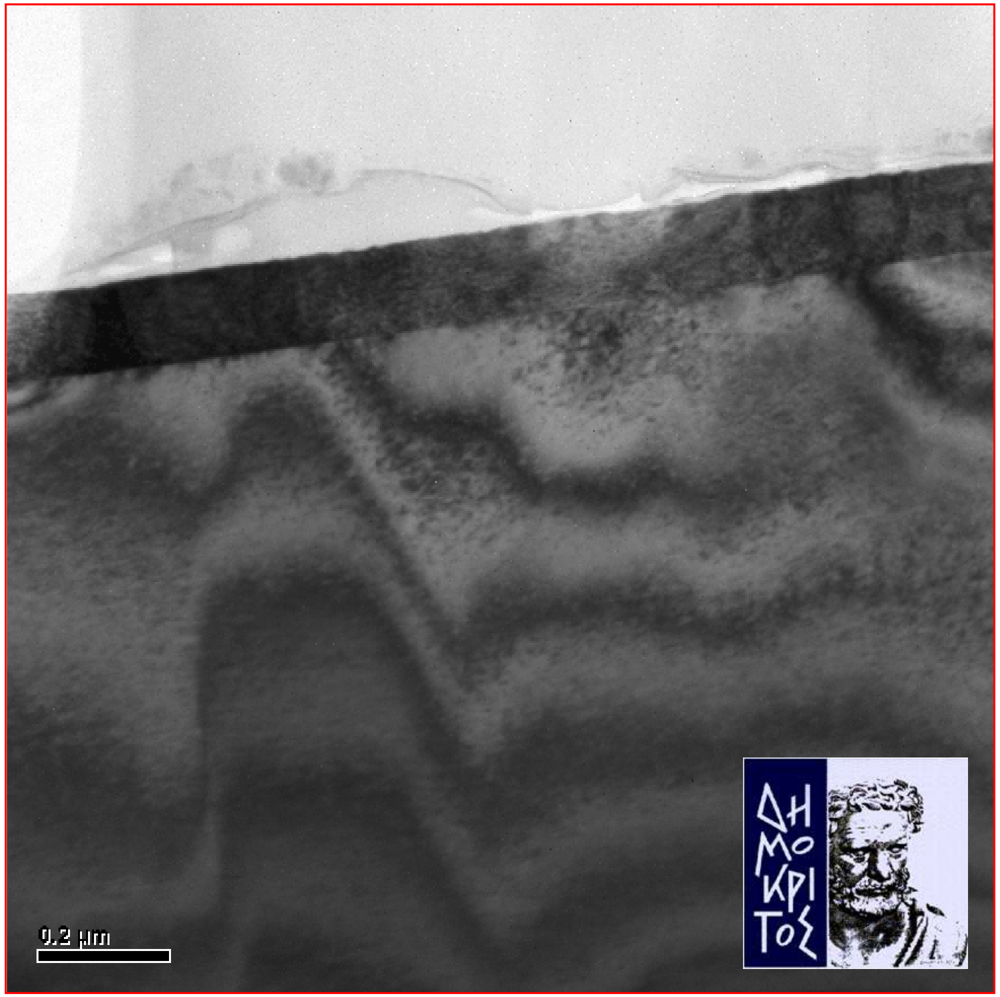
[Thermal processes (MBE & CVD) ➔ 0.1 – 1 eV]

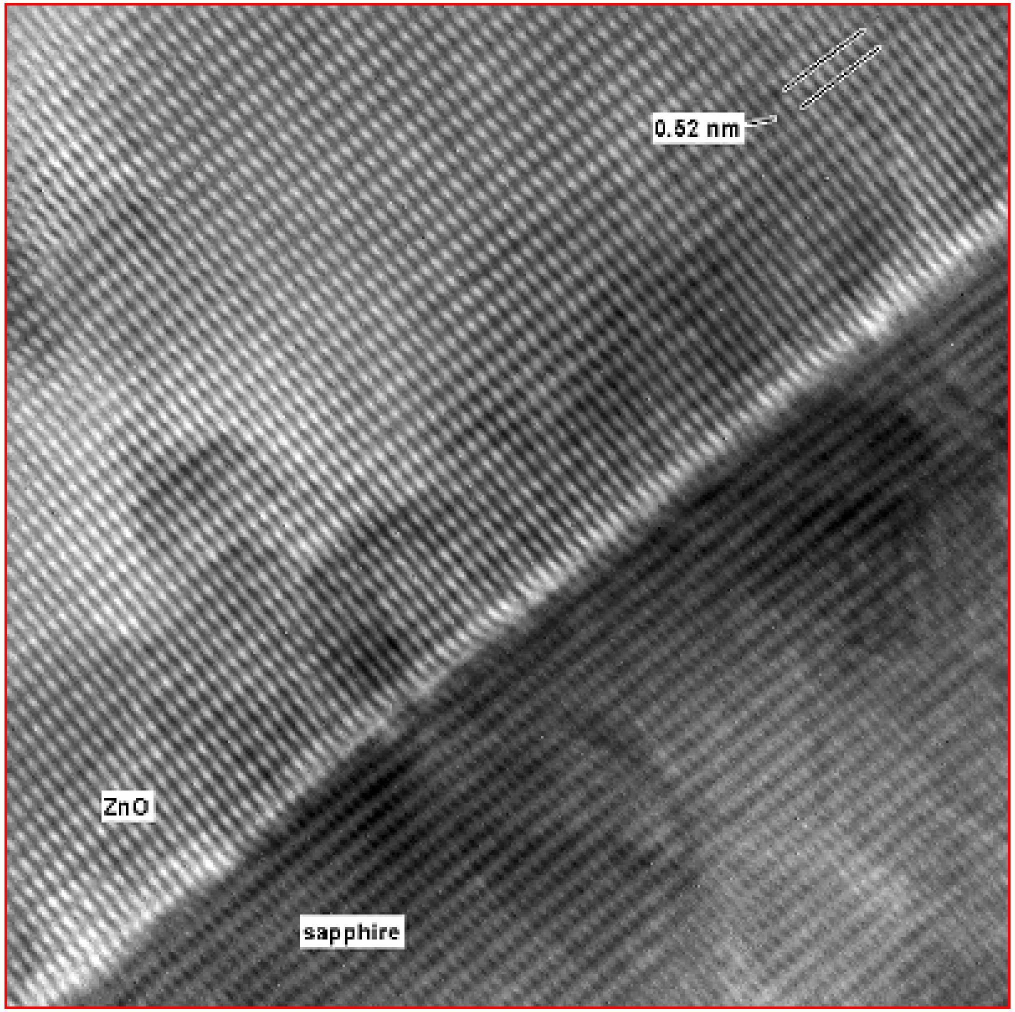
Can tune oxygen content via O pressure

Enhanced surface mobility/reactivity ➔ can crystallise well at low T

Rogers et al. Proc. of SPIE 7940 (2011) 79401K-1

HRTEM (Demokritos)

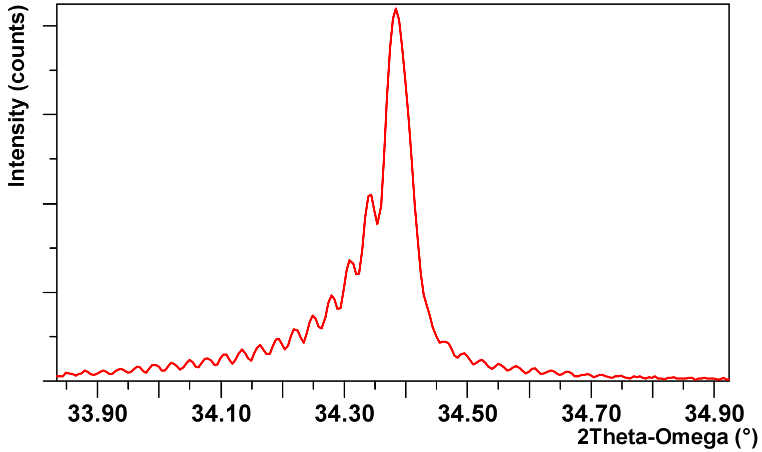


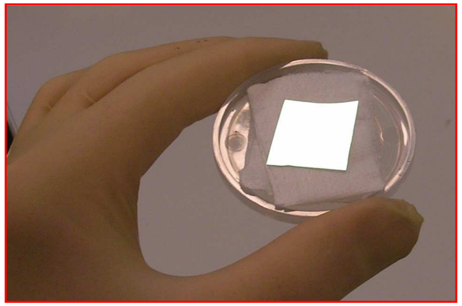


X-Ray Diffraction

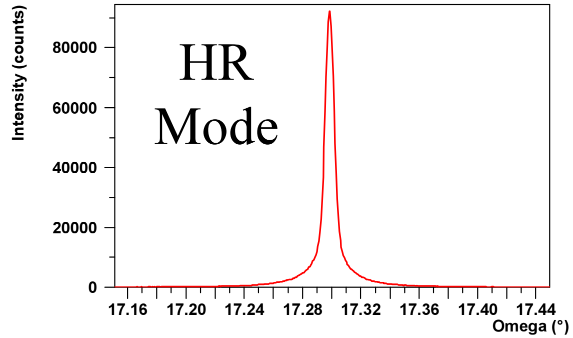
nanovation

XRD (0002) Peak 2Theta-Omega Scan

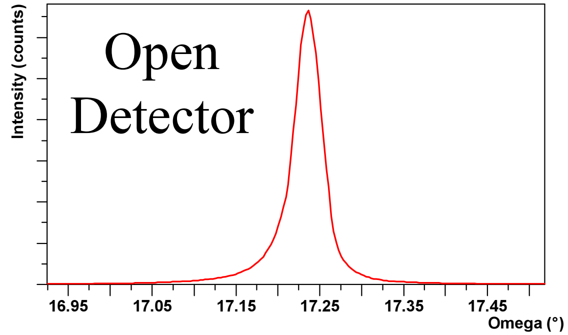




XRD (0002) Peak Omega Scans



FWHM = 0.0079°



FWHM = 0.039°

Rogers et al. Proc. SPIE 7217 (2009) 72170F-1

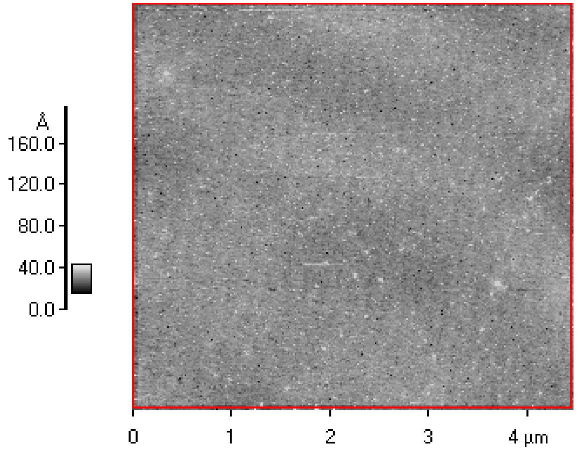
ZnO/Sapphire: AFM Measurements

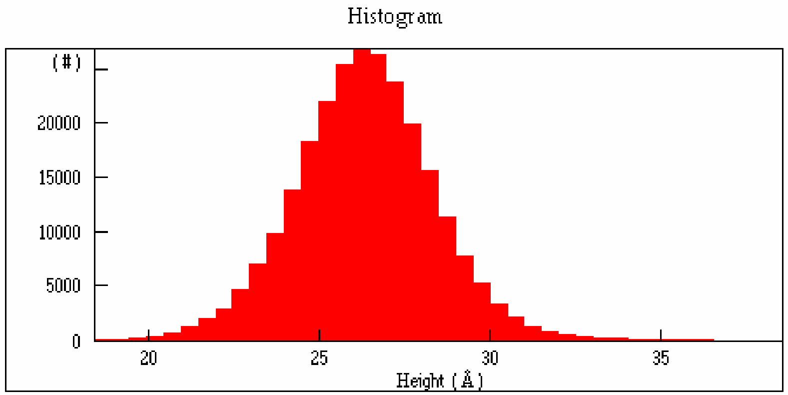
nanovation

Dec 16 104 s6c

Nanovation

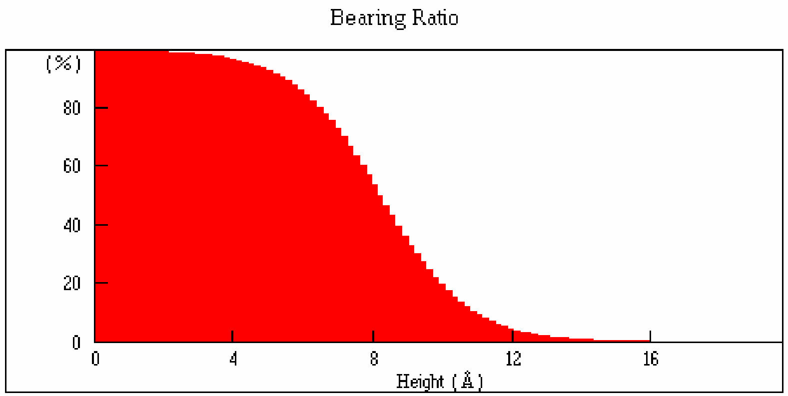
No Particulates





RMS Roughness = 2.3Å

Peak to Valley = 25Å

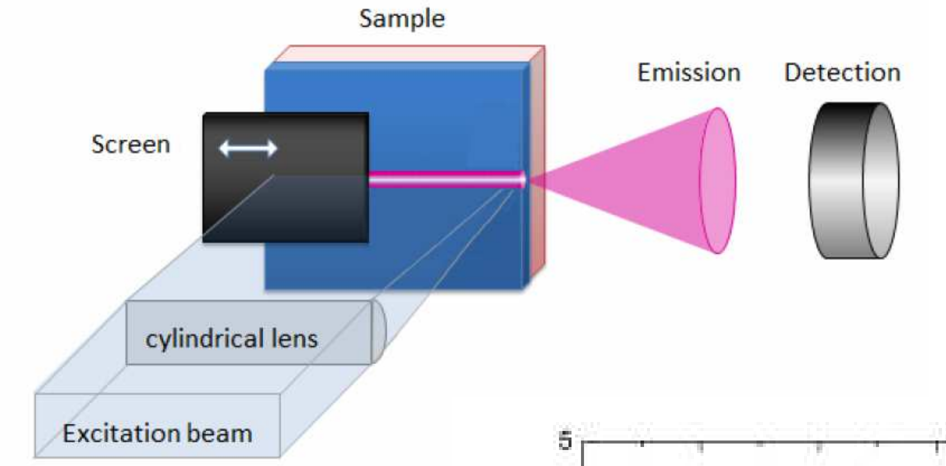


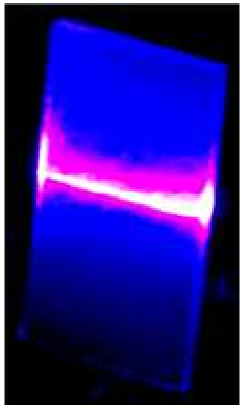
Institut d'Électronique Fondamentale

World Record Optical Gain for ZnO

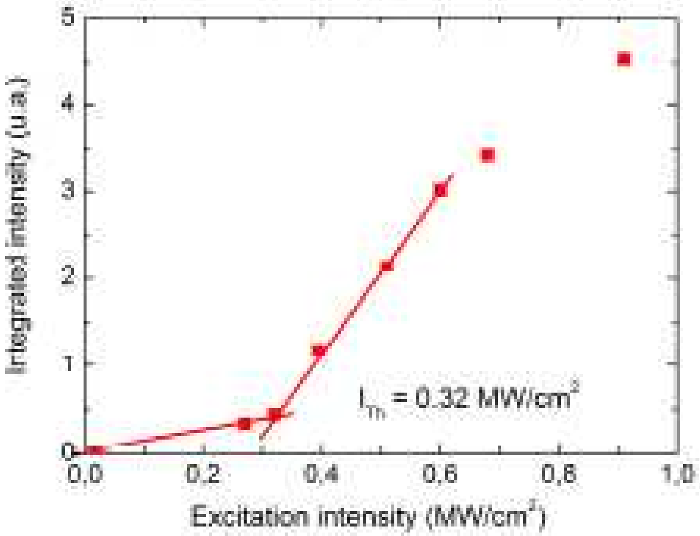
nanovation

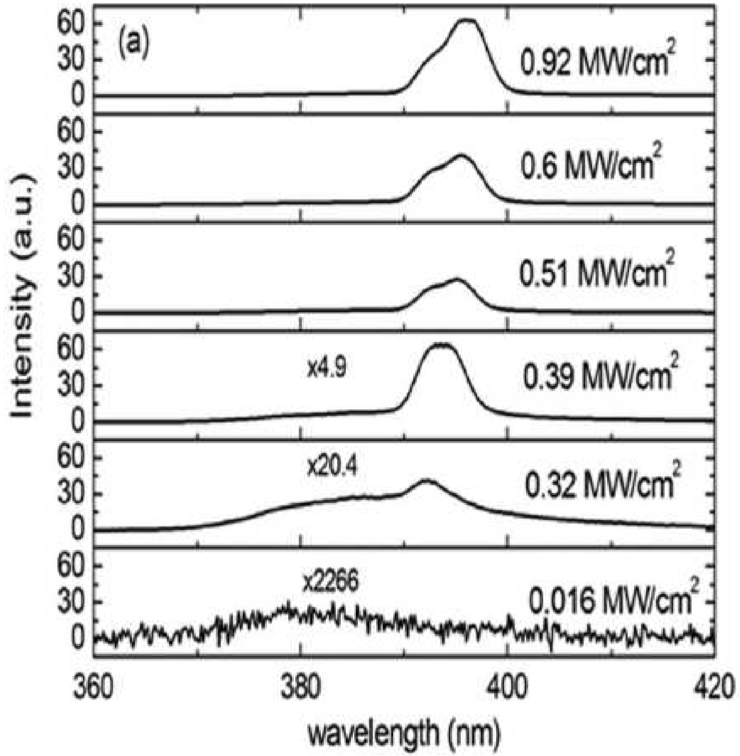
Variable Stripe Length Method





$$I_{ASE} = \frac{A}{g(\lambda)}[exp(g(\lambda)L) - 1]$$





500 nm thick sample…

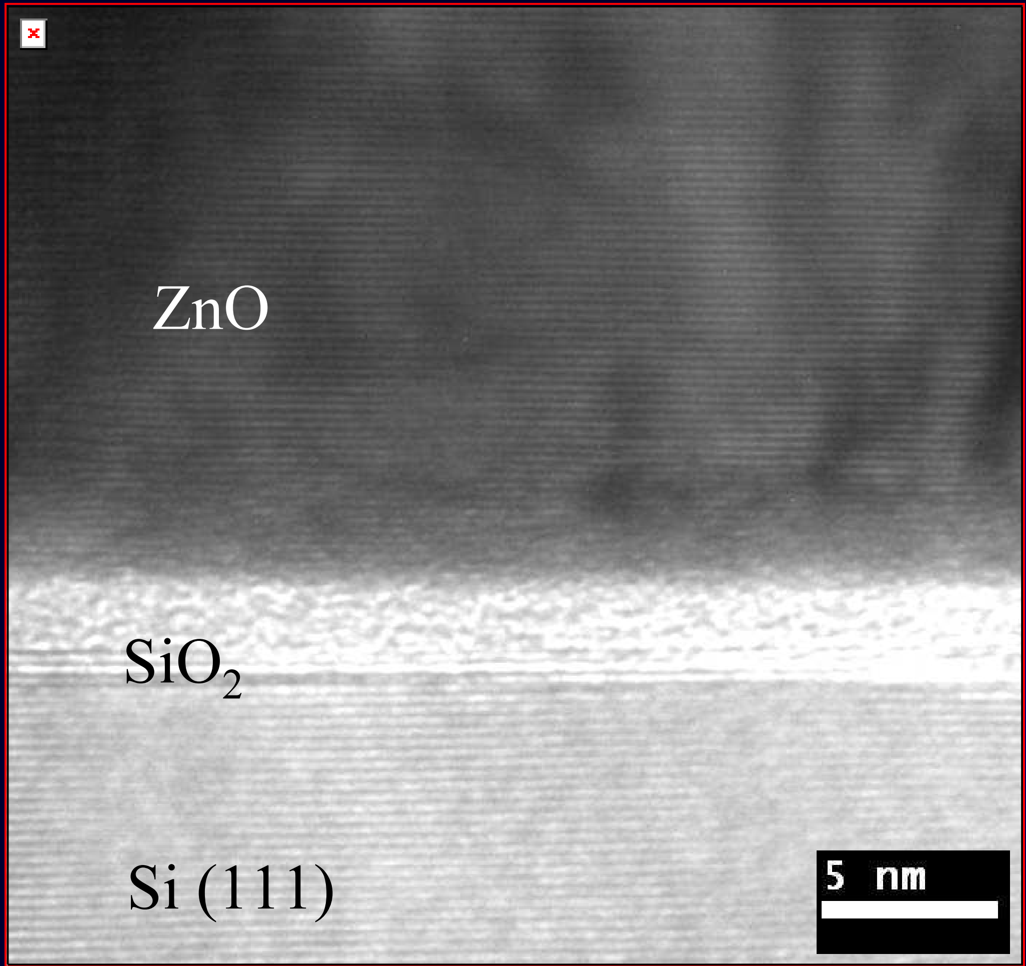
Gain > 1000 cm^{-1} …

utt université de technologie Troyes

Gadallah, Rogers et al. APL 102 (2013) 171105

$ZnO/a\text{-}SiO_2/Si$ (111) TEM

nanovation

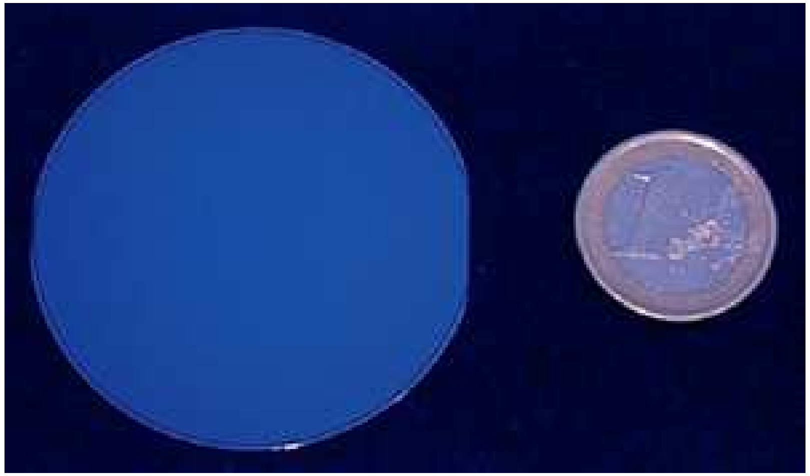


Coherent lattice fringes in ZnO after ~ 2nm of growth

Ougazzaden, Rogers et al. Proc. SPIE7603 (2010) 76031D-1

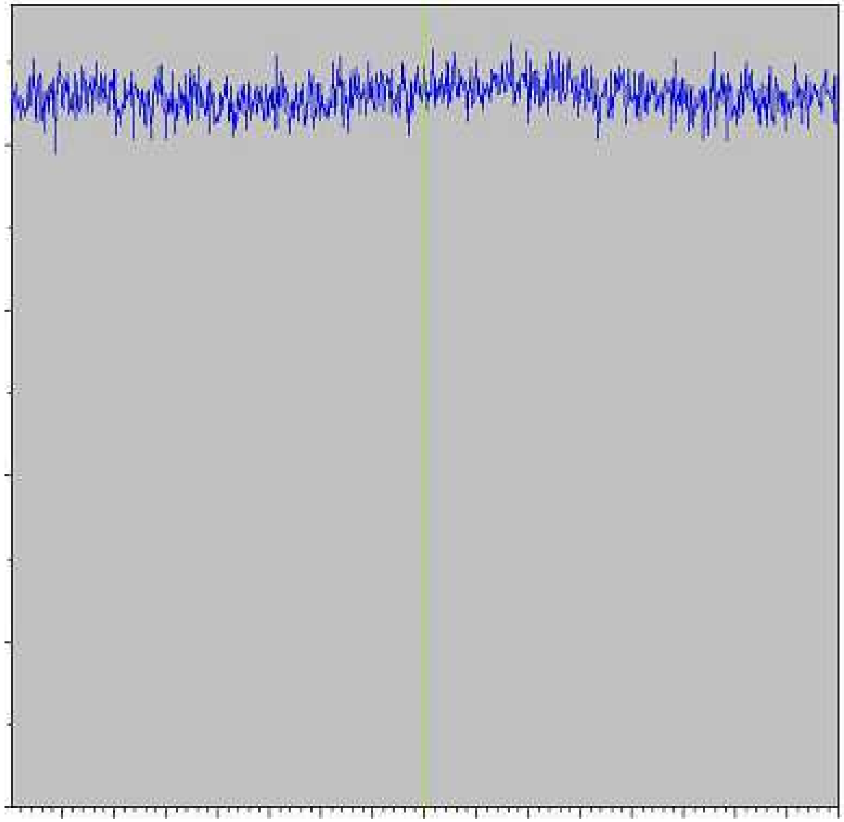
2 inch In-wafer Uniformity

nanovation



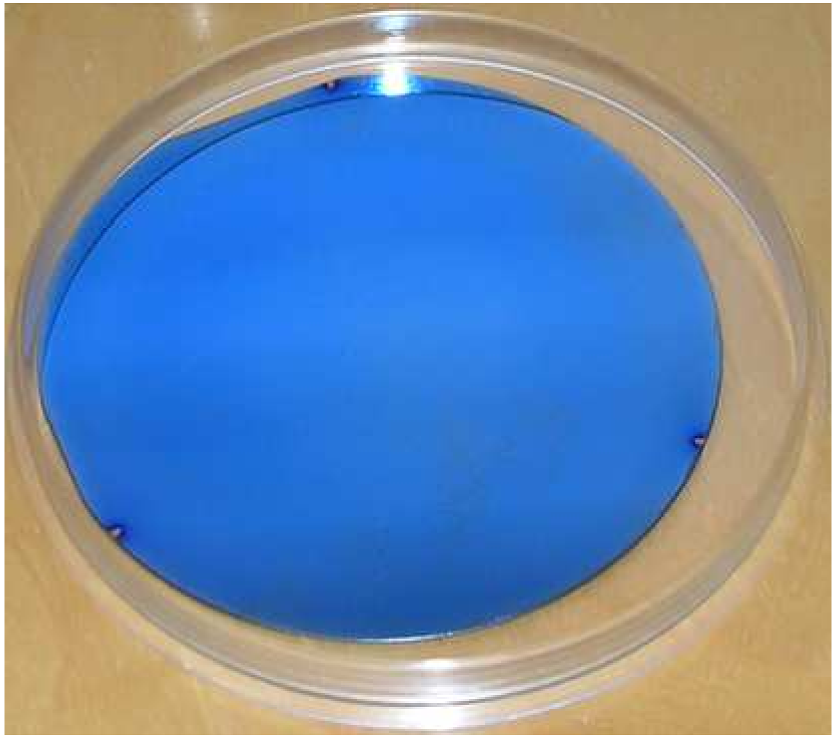
2 inch ZnO on Si

ZnO XRD (0002) Peak Intensity vs Position

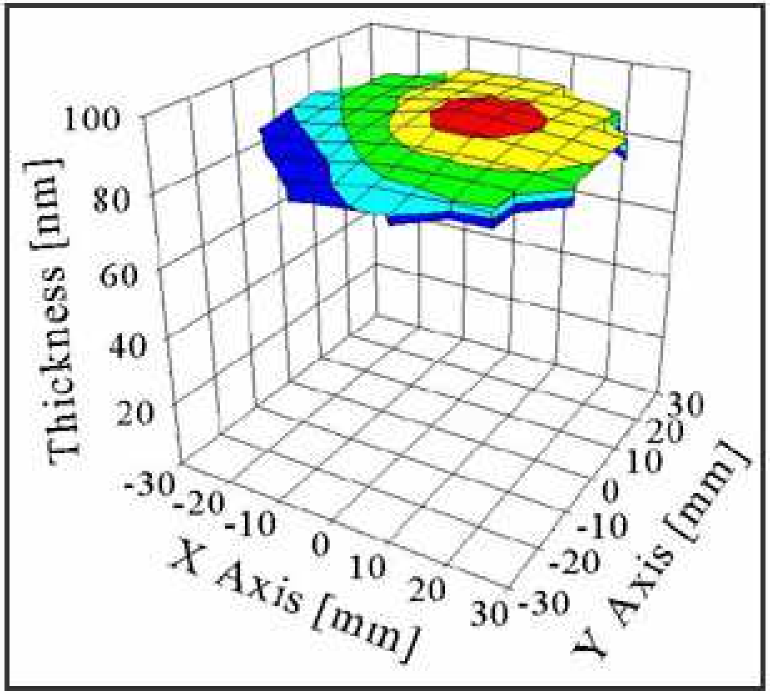


Gautier, Rogers et al. J. Cryst. Growth 370 (2013) 63

3 inch in-wafer Uniformity



75 mm



Self-forming Nanostructure Arrays by PLD

nanovation

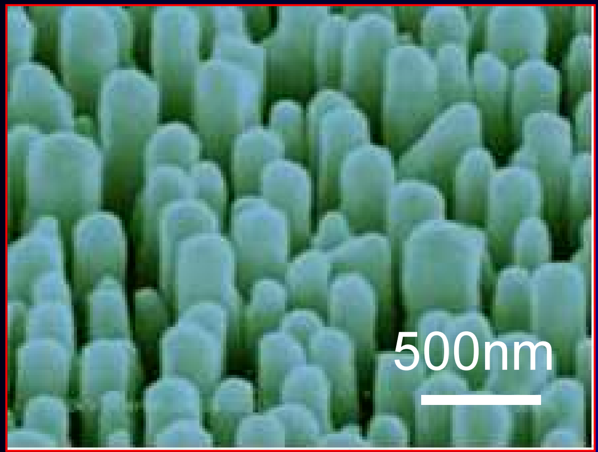
Energy Challenges & Mechanics
- working on small scales

Aug. 2015

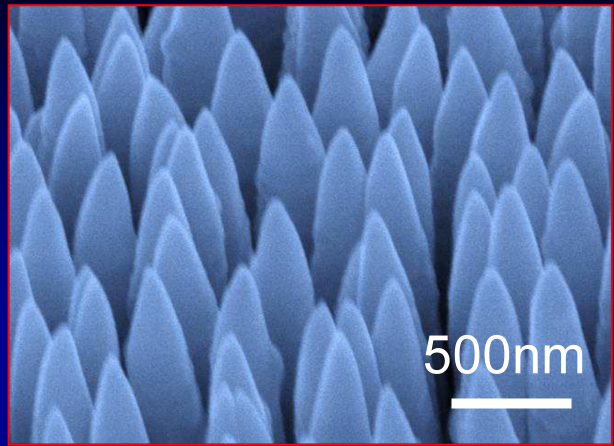
Nanoarrays by PLD Directly on Si

nanovation

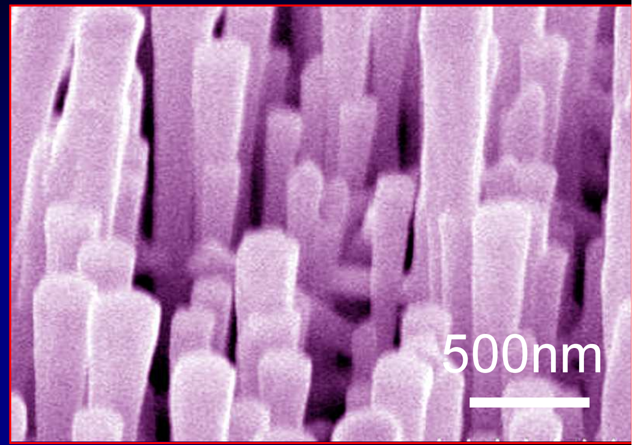
[Rogers et al. Proc. SPIE (2010)]



Nanorods



Moth-eye



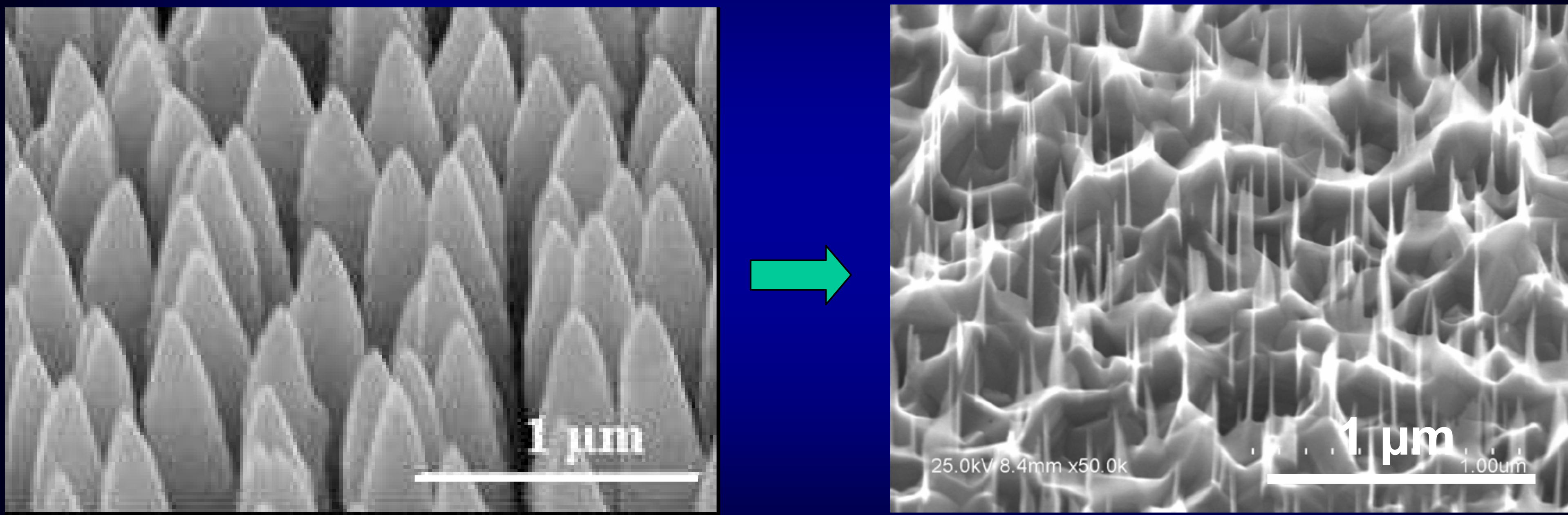
Broadening

Catalyst-free & self-forming!!!

Rogers et al. Proc. SPIE 7605 (2010) 76050K-1

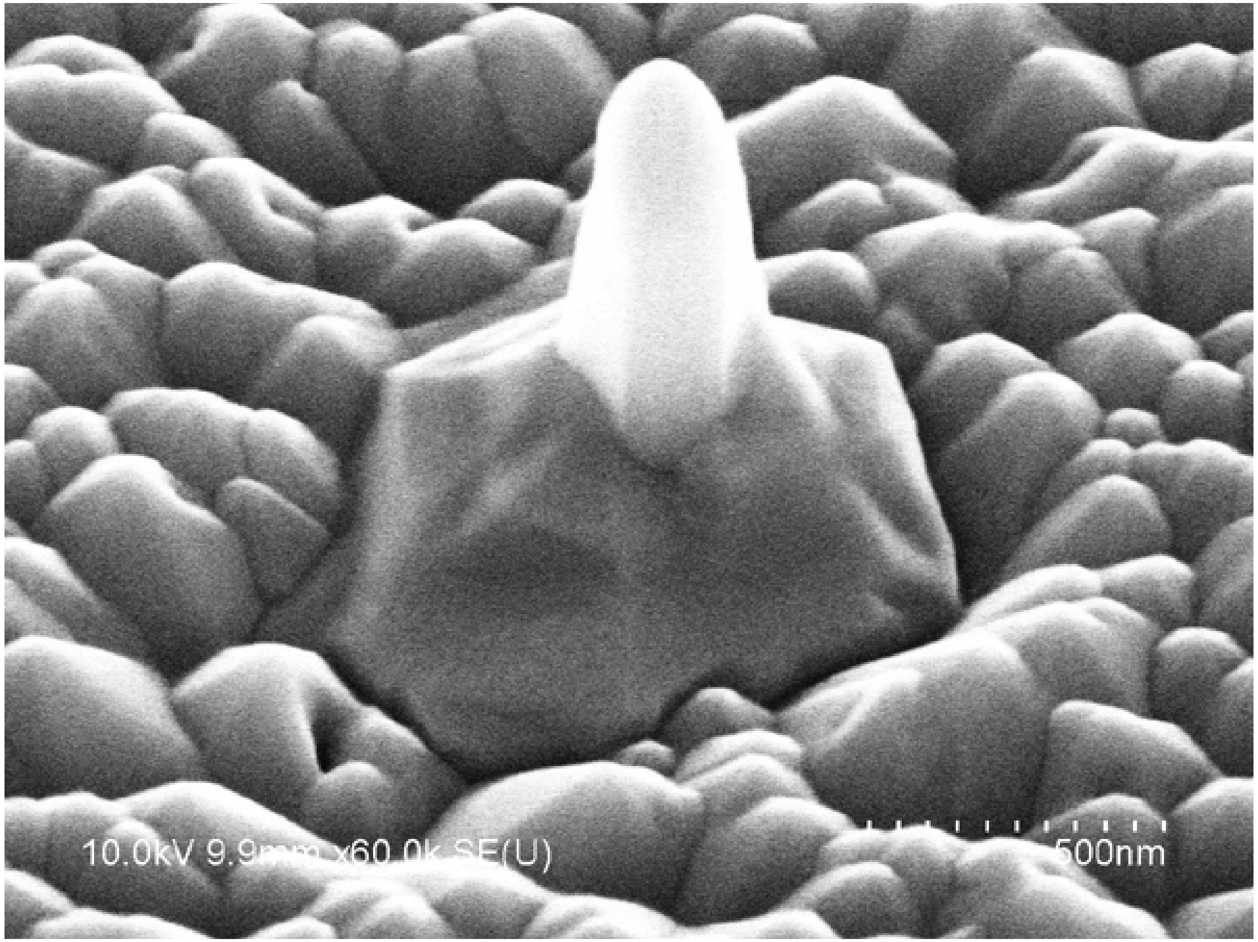
Nucleation/Growth Control → Much finer nanowires…

Increased Substrate Temperature



Sandana, Rogers et al. Phys. Status Solidi A 211,2 (2014) 449

Nanostructure pitch controlled by underlayer grain size



Sandana, Rogers et al. Phys. Status Solidi A 211,2 (2014) 449

Patterned Nanostructure Growth

nanovation

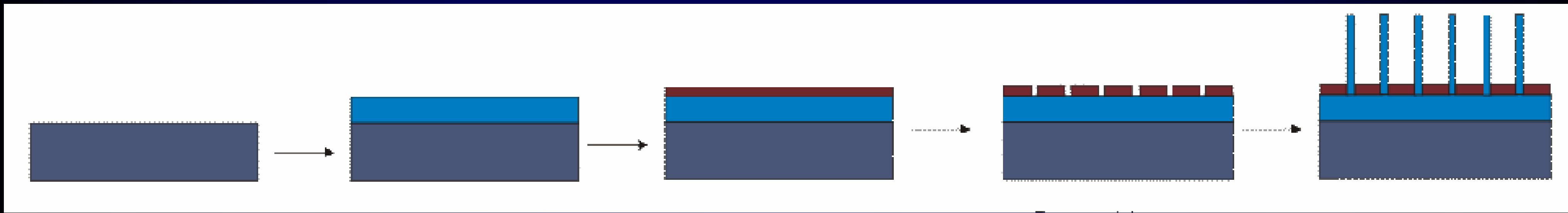
Energy Challenges & Mechanics
- working on small scales

Aug. 2015

Difficult to Grow Regular Nano ZnO by PLD

nanovation

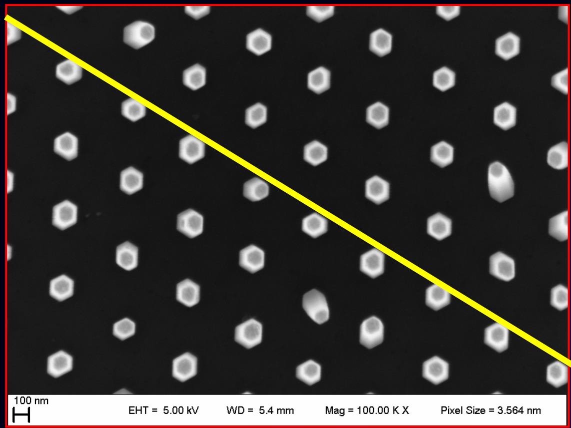
➔ Use PLD Layer as Template



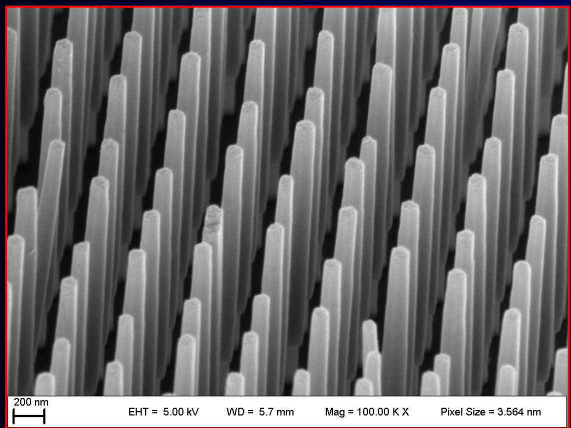
Substrate | **PLD ZnO** | **Spin on Resist** | **E-beam Lithography** | **Wet Chemical Nanowire Growth**

Erdelyi, Rogers et al. Cryst Growth & Design 11 (2011) 2515

Wet Chemical Arrays on e-beam Patterned Seed Layers… nanovation

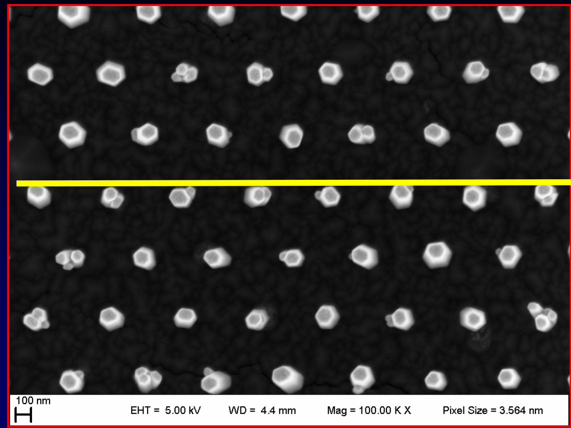


Facets Aligned!

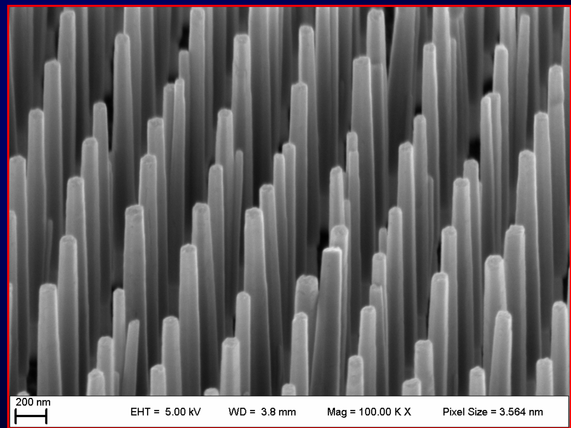


500nm

ZnO/sapphire



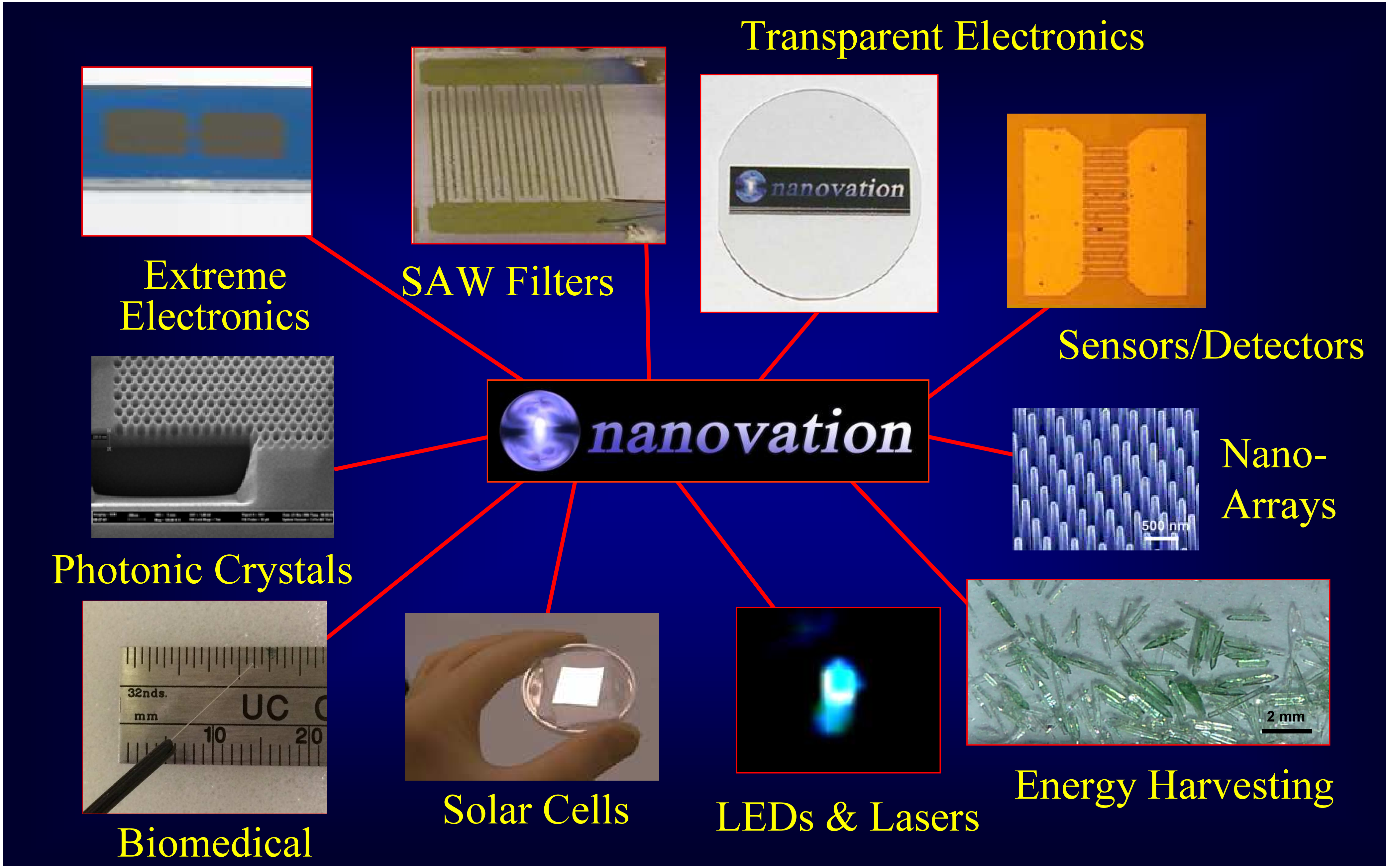
Facets Not Aligned



500nm

ZnO/a-SiO_2/Si

Erdelyi, Rogers et al. Cryst Growth & Design 11 (2011) 2515


Transparent Electronics
nanovation
Extreme Electronics
SAW Filters
Sensors/Detectors
nanovation
Nano-Arrays
500 nm
Photonic Crystals
Energy Harvesting
2 mm
32nds.
mm
UC
10
20
Biomedical
Solar Cells
LEDs & Lasers

3. ZnO in Solar Energy Harvesting

Transparent Conducting Electrodes for Solar Cells

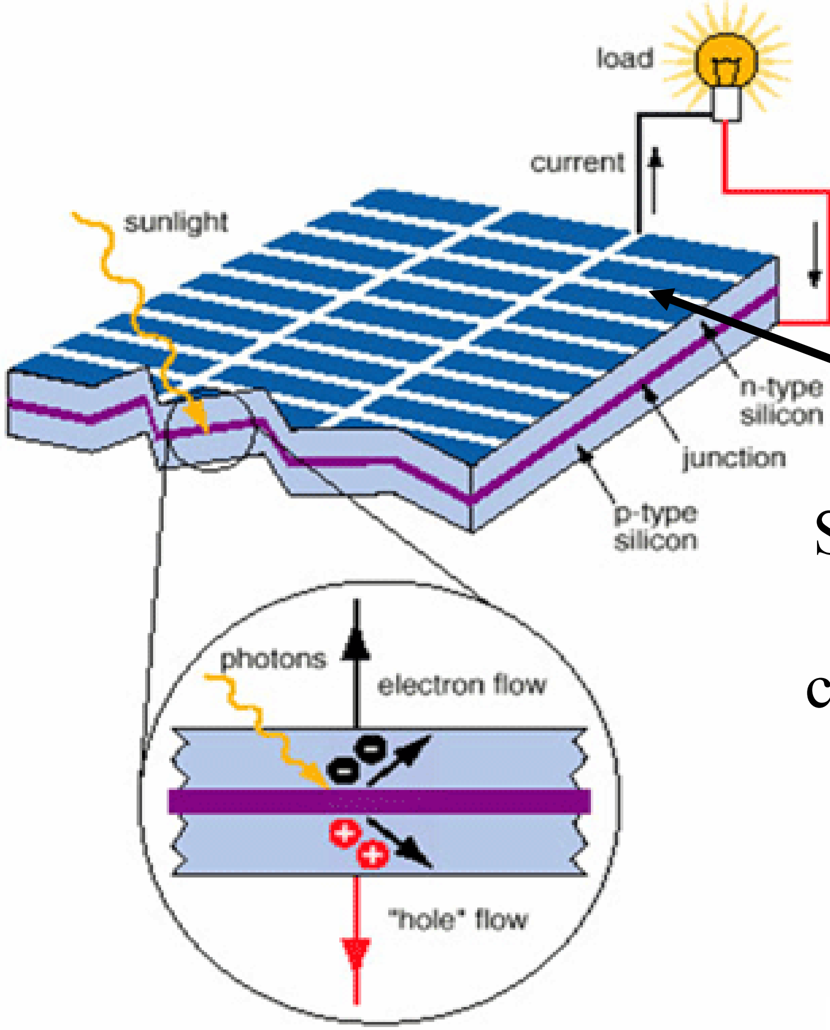
Rogers & Hosseini Teherani, Elsevier Encyclopedia of Materials Science, Oxford (2010) 1

nanovation

Energy Challenges & Mechanics
- working on small scales

Aug. 2015

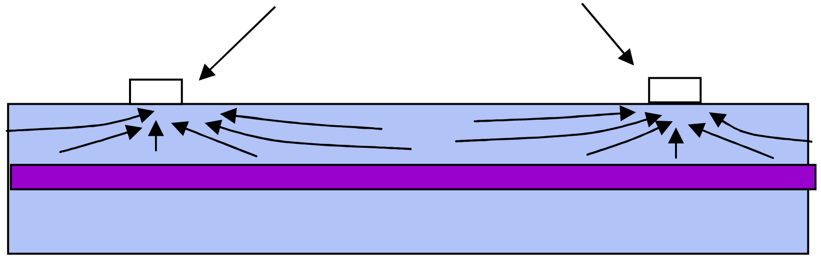
Conventional Si Solar Cell



Surface metallic grid for current collection

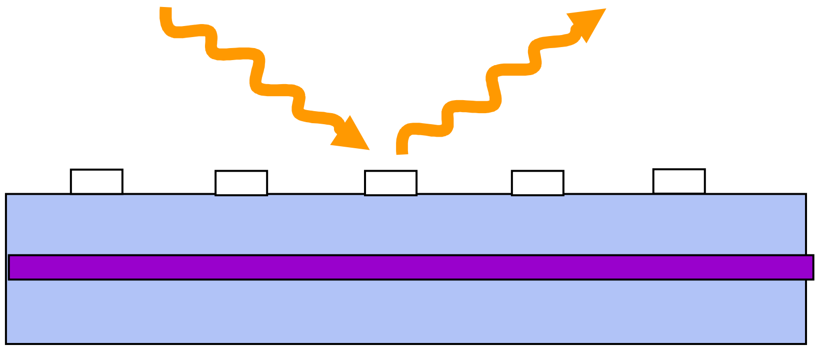
Why do we need a TCO layer?

Metallic electrode grid

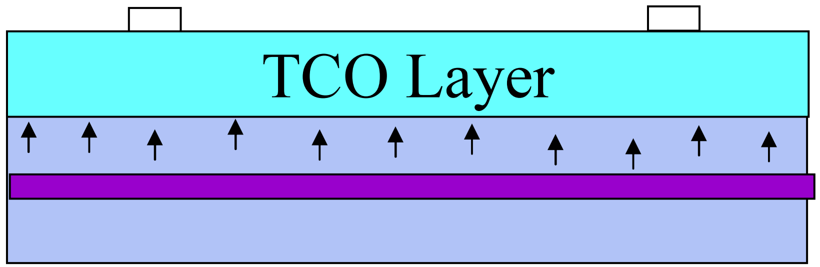


- Current crowding
- Electric field generation in active layer
- Recombination & resistance losses

Higher Density Metallic electrode grid



- lots of reflection losses



- R_{TCM} << R active layer
- TCO relatively equipotential
- charges prefer to propagate in TCO

Transparent Electrode: Minimum Requirements

1) resistivity $\leq 10^{-3}\ \Omega$cm

2) carrier concentration $\geq 10^{20}$ cm^{-3}

3) average transmittance $\geq$ 80% in the visible

4) Eg > 3 eV: i.e., degenerate n-type or p-type

UNIVERSITY OF OXFORD

T. Minami, Semicond. Sci. Technol. 20 (2005) S35–S44

Some Potential TCOs for use as Contacts

nanovation

Material	Dopant or compound
SnO_2	Sb, F, As, Nb, Ta
In_2O_3	Sn, Ge, Mo, F, Ti, Zr, Hf, Nb, Ta, W, Te
ZnO	Al, Ga, B, In, Y, Sc, F, V, Si, Ge, Ti, Zr, Hf
CdO	In, Sn
$ZnO–SnO_2$	Zn_2SnO_4, $ZnSnO_3$
$ZnO–In_2O_3$	$Zn_2In_2O_5$, $Zn_3In_2O_6$
$In_2O_3–SnO_2$	$In_4Sn_3O_{12}$
$CdO–SnO_2$	Cd_2SnO_4, $CdSnO_3$
$CdO–In_2O_3$	$CdIn_2O_4$
$MgIn_2O_4$	
$GaInO_3$, $(Ga, In)_2O_3$	Sn, Ge
$CdSb_2O_6$	Y
$ZnO–In_2O_3–SnO_2$	$Zn_2In_2O_5–In_4Sn_3O_{12}$
$CdO–In_2O_3–SnO_2$	$CdIn_2O_4–Cd_2SnO_4$
$ZnO–CdO–In_2O_3–SnO_2$	

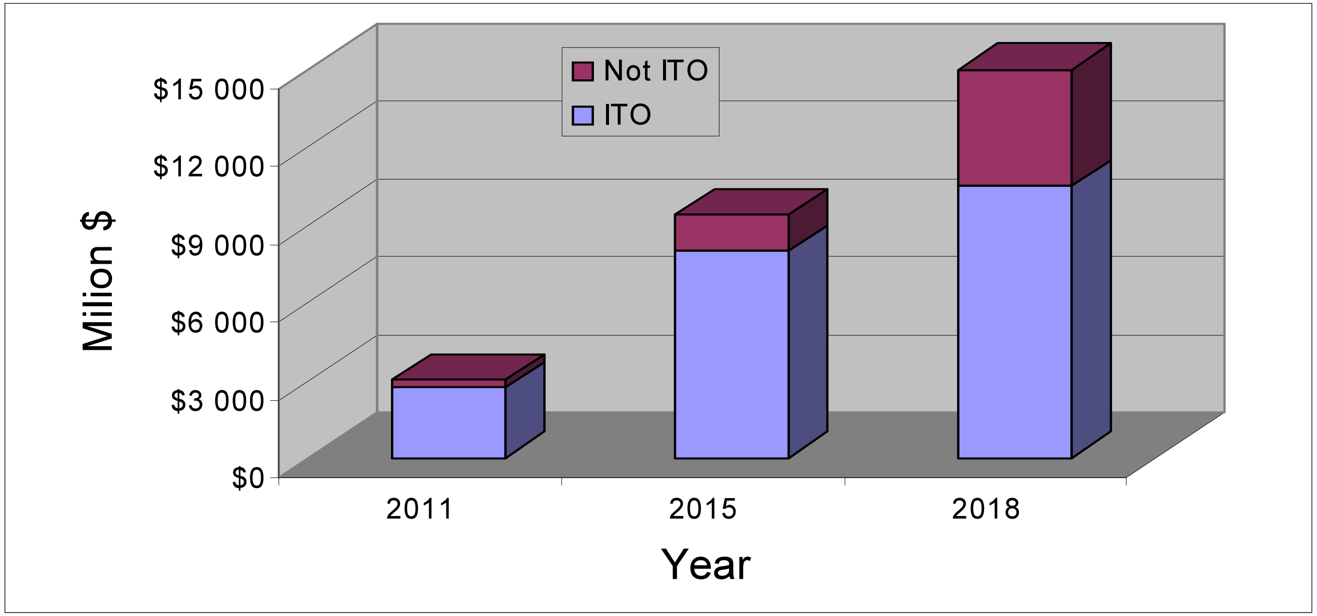
Which to choose?

T. Minami, Semicond. Sci. Technol. 20 (2005) S35–S44

Transparent Elecrode Market

nanovation

Sputtered ITO in use for most transparent electrode applications



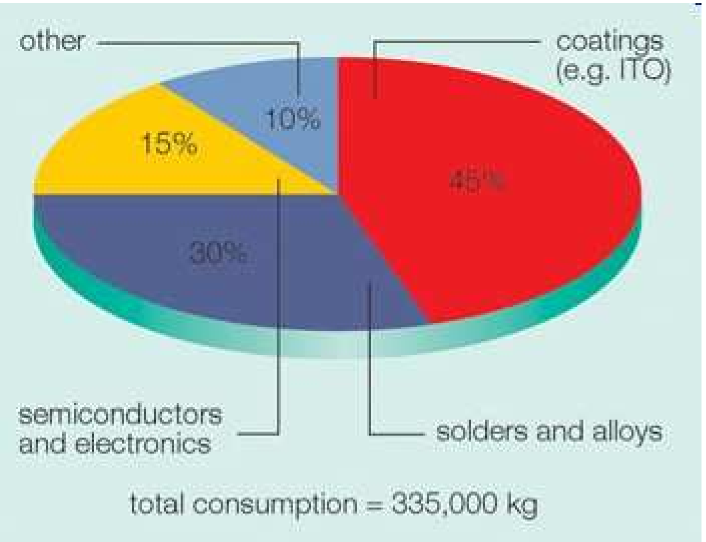
Indium Tin Oxide (ITO)
90% ➔70% of market in 2018

Why is there a drive to replace ITO?

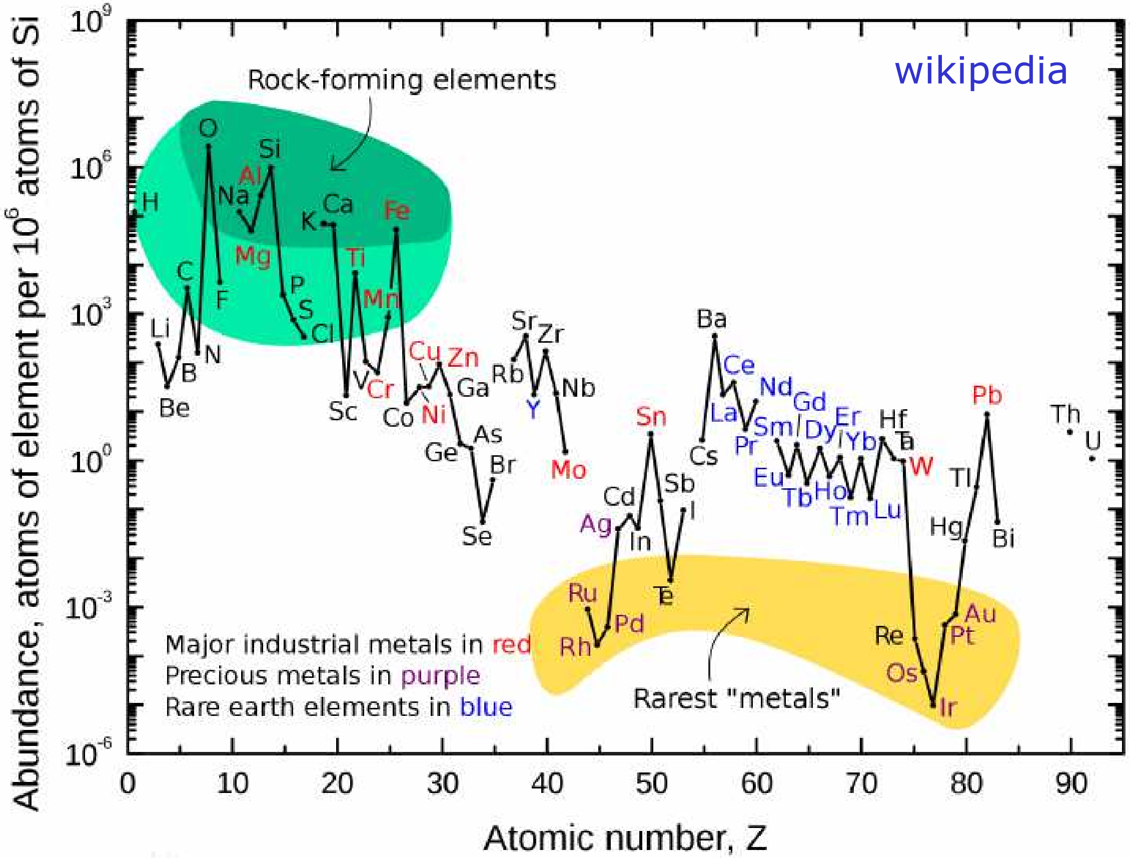
Sandana, Rogers et al. Proc. of SPIE Vol. 8626 (2013) 862603-1

Problems with ITO: 1. Scarcity of Indium

- 61st element in earth's crust: 0,24 ppm
- Use rising ➔ price rising



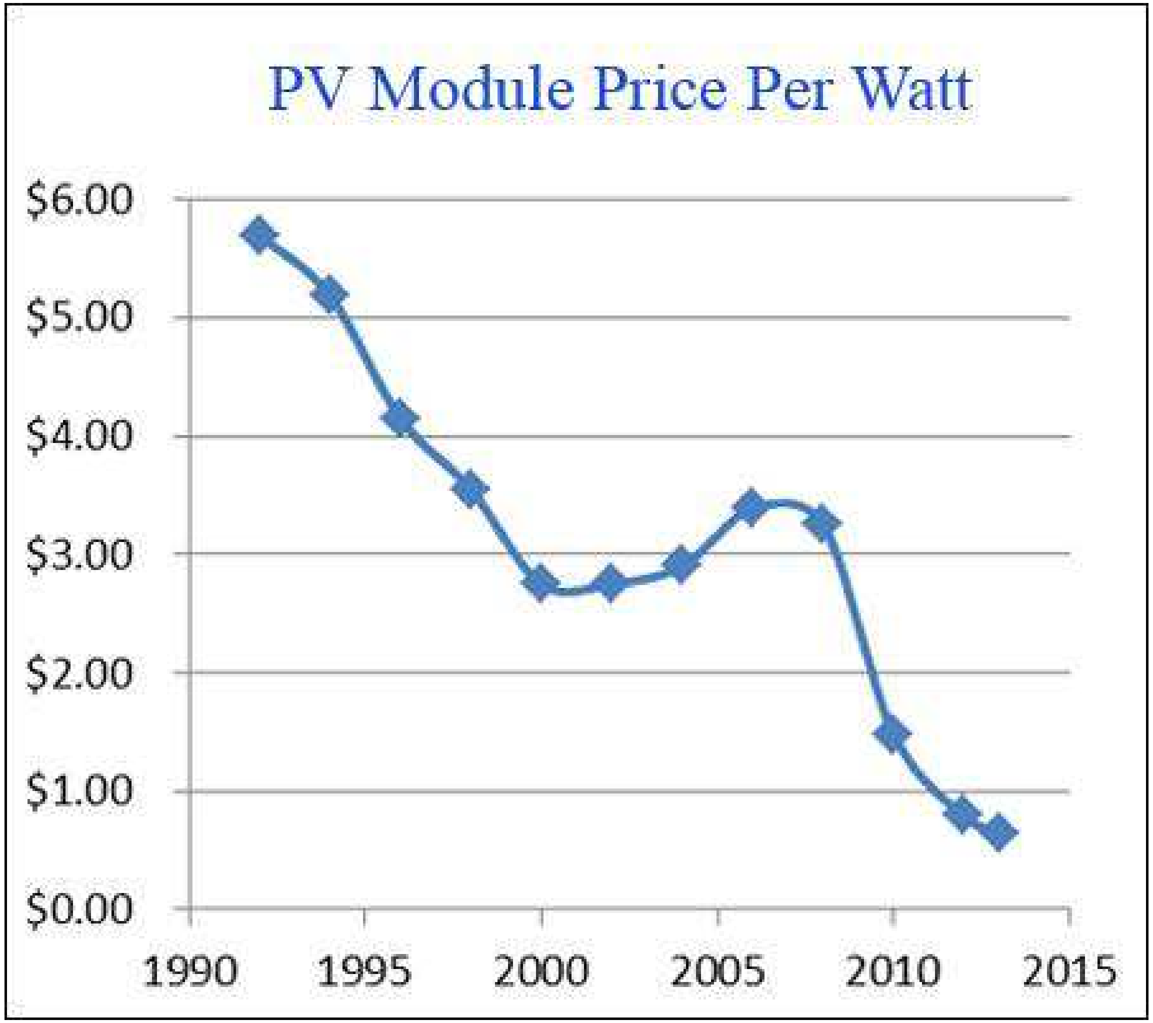
Compound Semiconductor Magazine



Transparent Conductor Cost Levels

~$7/m^2$
≈ 10% of PV fabrication price
Source: J. Kalowekamo et al.
Sol. Energy (2009)

Dramatic Solar Cell Price Drop



Puts pressure on TCO price…

www.solarcellcentral.com

Problems with ITO: 2. Toxicity of Indium

Indium based compounds are carcinogenic & toxic (they attack the heart, liver, kidneys…)

Problems with ITO: 3. Specialised Contact Needs…

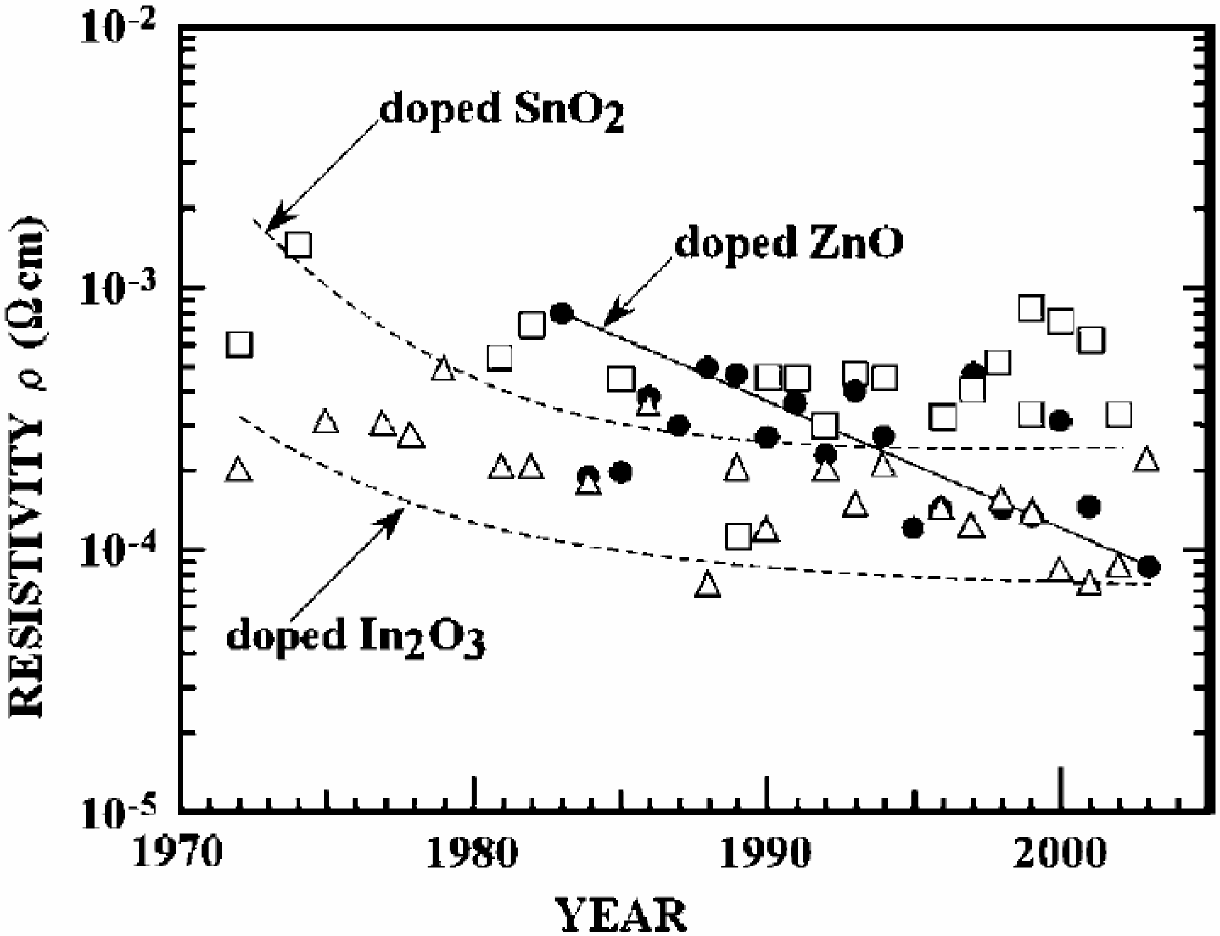
Choice of Transparent Conductors.

Property	Material
Highest transparency	$ZnO:F$, Cd_2SnO_4
Highest conductivity	$In_2O_3:Sn$
Lowest plasma frequency	$SnO_2:F$, $ZnO:F$
Highest plasma frequency	Ag, TiN, $In_2O_3:Sn$
Highest work function, best contact to *p*-Si	$SnO_2:F$, $ZnSnO_3$
Lowest work function, best contact to *n*-Si	$ZnO:F$
Best thermal stability	$SnO_2:F$, TiN, Cd_2SnO_4
Best mechanical durability	TiN, $SnO_2:F$
Best chemical durability	$SnO_2:F$
Easiest to etch	$ZnO:F$, TiN
Best resistance to H plasmas	$ZnO:F$
Lowest deposition temperature	$In_2O_3:Sn$, $ZnO:B$, Ag
Least toxic	$ZnO:F$, $SnO_2:F$
Lowest cost	$SnO_2:F$

Source: Gordon, MRS Bulletin, 2000

Resistivity Evolution: ZnO, SnO_2 & In_2O_3

nanovation



1) Minimum ρ for doped ZnO still decreasing

2) Minimum ρ for doped SnO_2 & In_2O_3 flat for ~ 20 years now

3) Minimum $\rho < 10^{-4}$ Ω.cm now reported for both ITO & ZnO

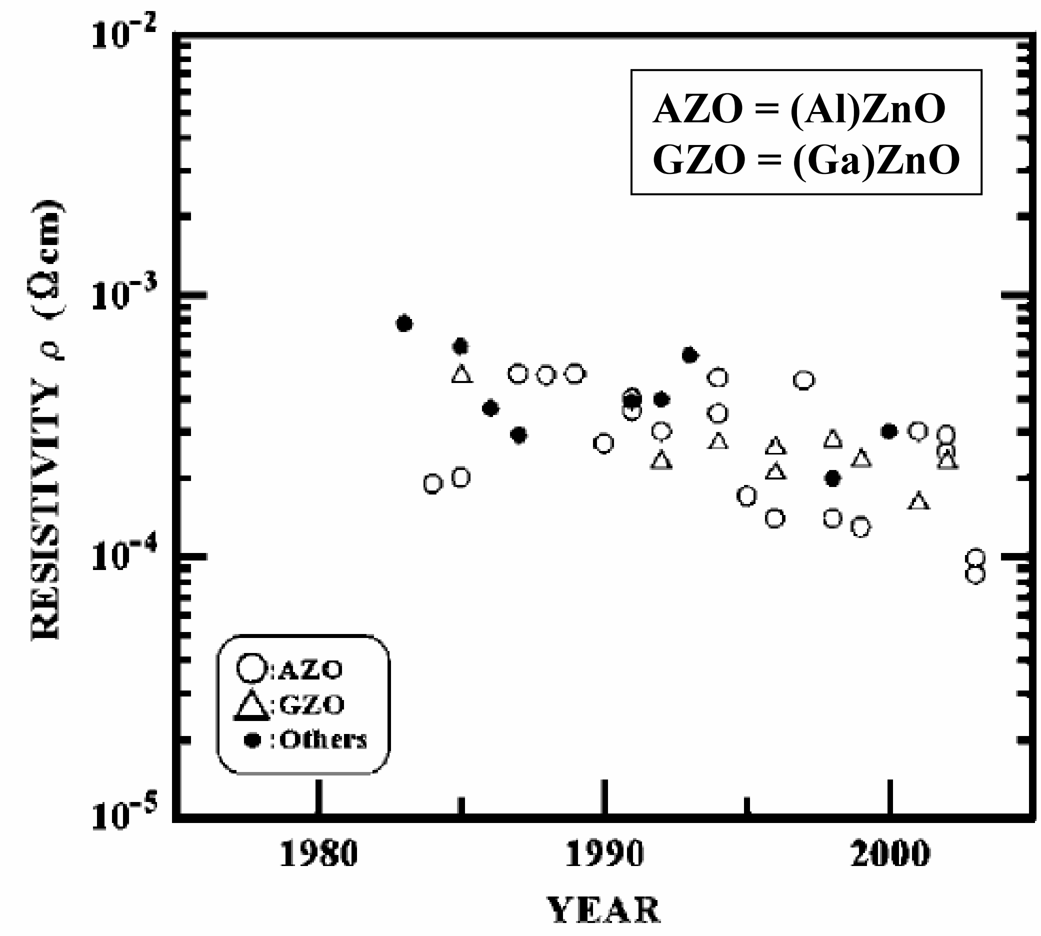
T. Minami, Semicond. Sci. Technol. 20 (2005) S35–S44

nanovation

Energy Challenges & Mechanics - working on small scales

Aug. 2015

Lowest Resistivities Attained for ZnO Dopants



Dopant	Dopant content (wt%)	Resistivity × 10^{-4} (Ω cm)	Carrier concentration × 10^{20} (cm^{-3})
Al_2O_3	1–2	0.85	15.0
Ga_2O_3	2–7	1.2	14.5
B_2O_3	2	2.0	5.4
Sc_2O_3	2	3.1	6.7
SiO_2	6	4.8	8.8
V_2O_5	0.5–3	5.0	4.9
F	0.5 (at%)	4.0	5.0
None	0	4.5	2.0

T. Minami, Semicond. Sci. Technol. 20 (2005) S35–S44

AZO Comparable to ITO but Lower Cost…

Record Breaking AZO by PLD:

	Doped ZnO	ITO
Low resistivity (Ω cm)	10^{-5}	10^{-5}
Practical resistivity (Ω cm)	$2–3 \times 10^{-4}$	1×10^{-4}
E_g (eV)	3.3	3.7
Index of refraction	2	2
Work function	4.6	4.8–5.0
Cost	Inexpensive	Very expensive
Stability		
Acid solution	<Good (stable)	
Alkali solution	<Good (stable)	
Oxidizing atmosphere at high temperature (or oxygen plasma)	<Good (stable)	
Reducing atmosphere at high temperature (or hydrogen plasma)	Good (stable)>	

Minami, Semicond. Sci. Technol. ***20*** *(2005) 35*

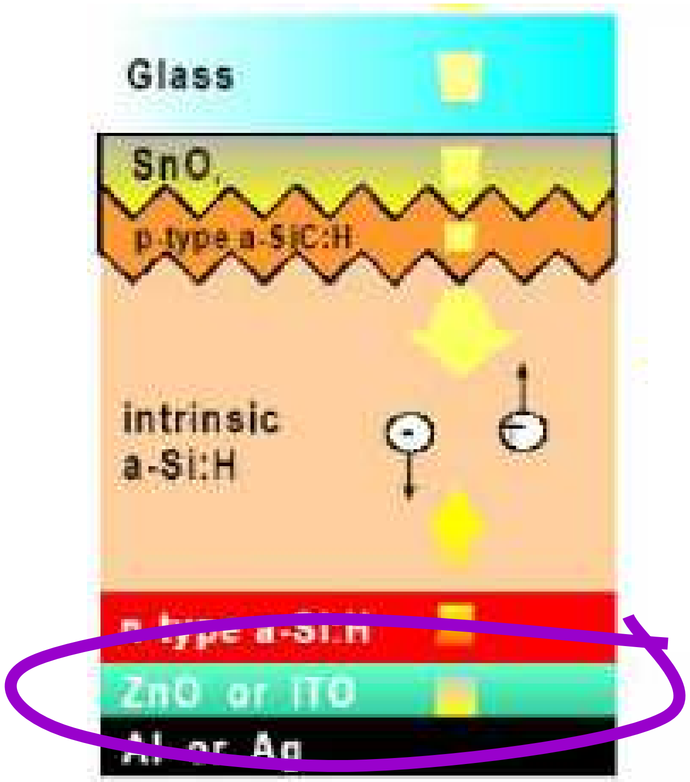
ZnO Multifunctionality in Solar Cells

nanovation

Energy Challenges & Mechanics
- working on small scales

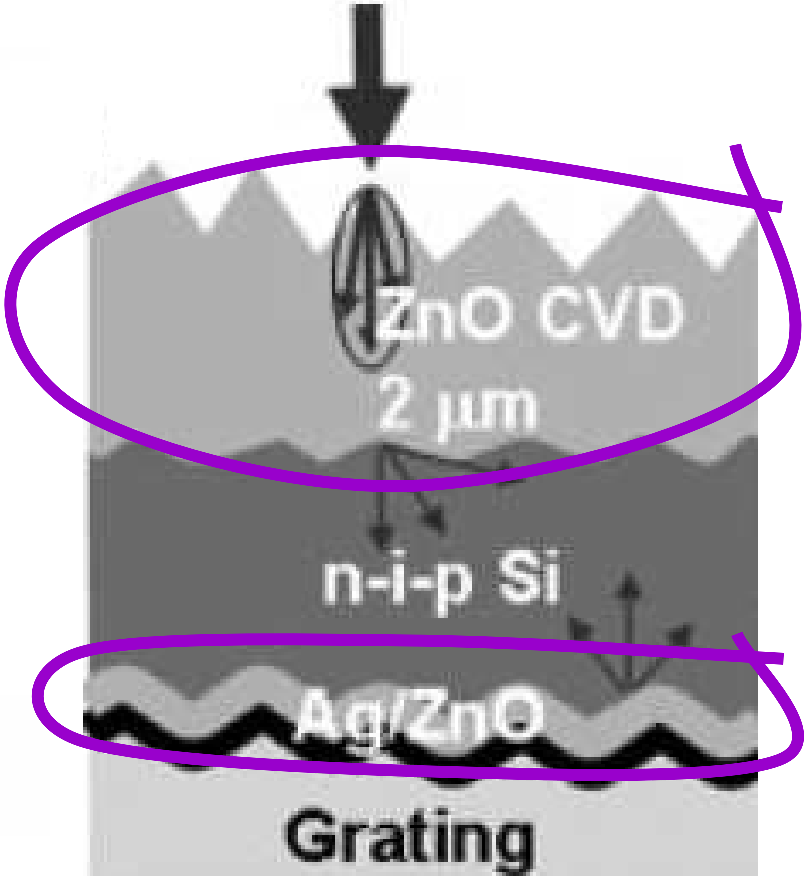
Aug. 2015

Amorphous Silicon (a-Si) PV



Oerlikon Solar

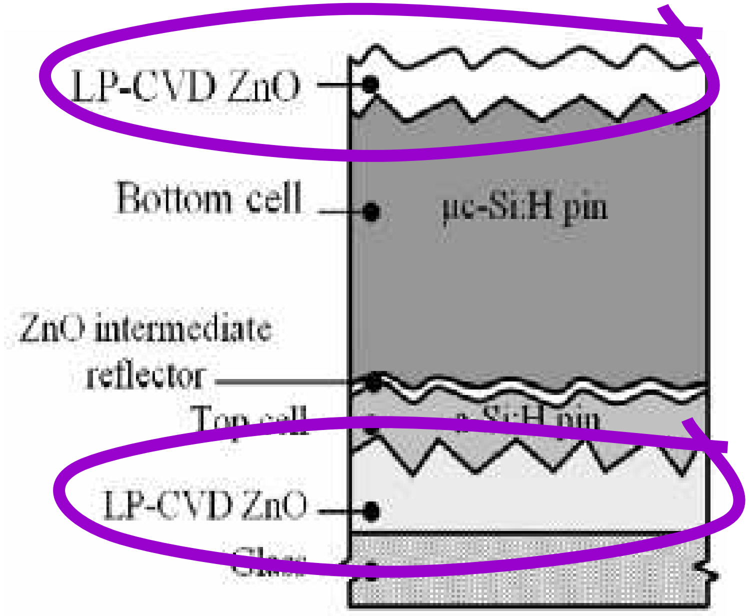
Micro-Crystalline (μ-c) Silicon



D. Domine et al., IMT, 2005

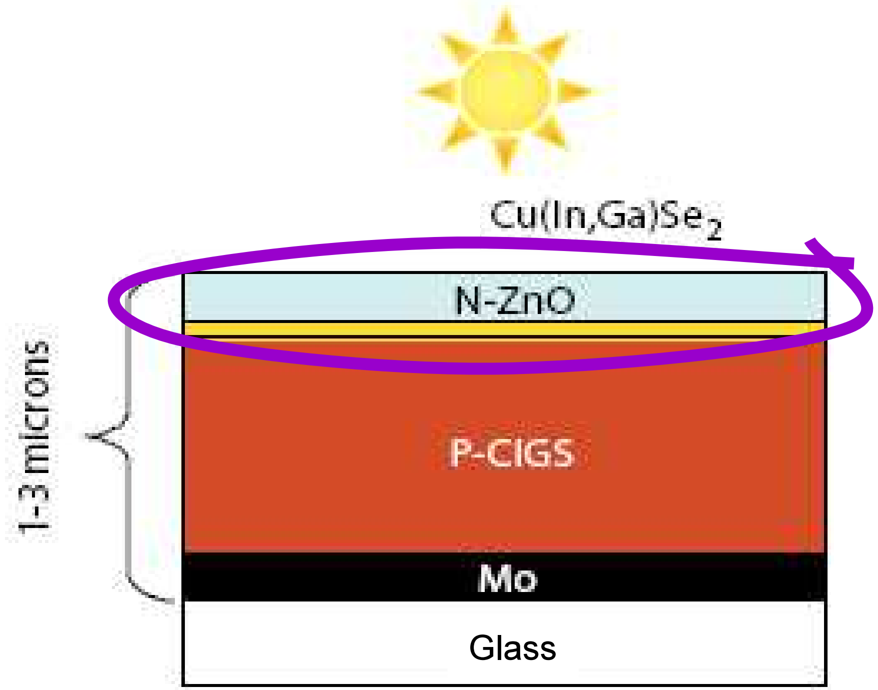
Spot the TCM…

Tandem Cell: μ-c Silicon / a-Si



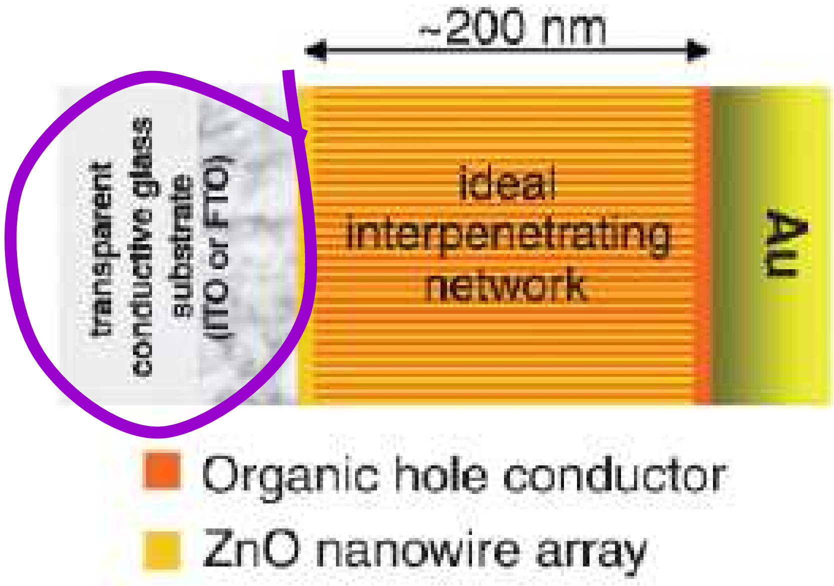
Soderstrom et al. Prog. Photovolt: Res. Appl. (2008)

CIGS ($Cu(InGa)Se_2$)



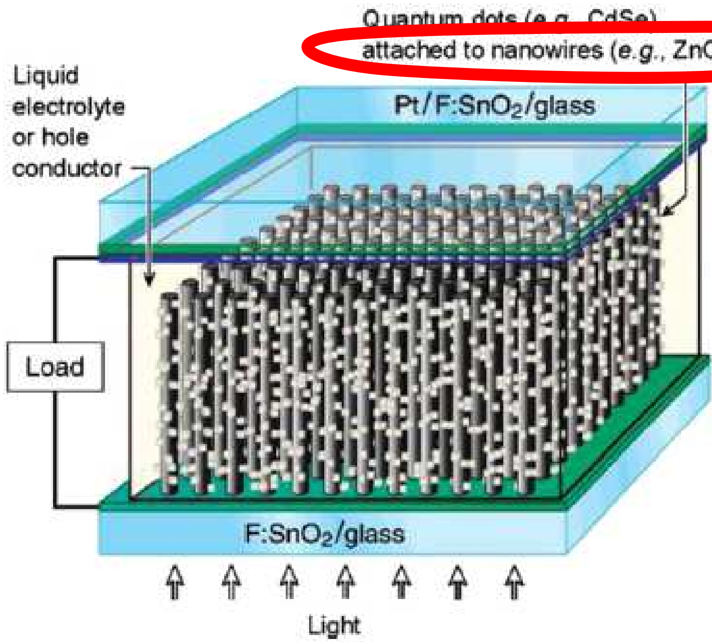
O. Durand, INSA Rennes

Hybrid Organic/Inorganic Solar Cell



NREL

Quantum Dot Sensitized Solar Cell



Li et al., Nanoenergy (2012)

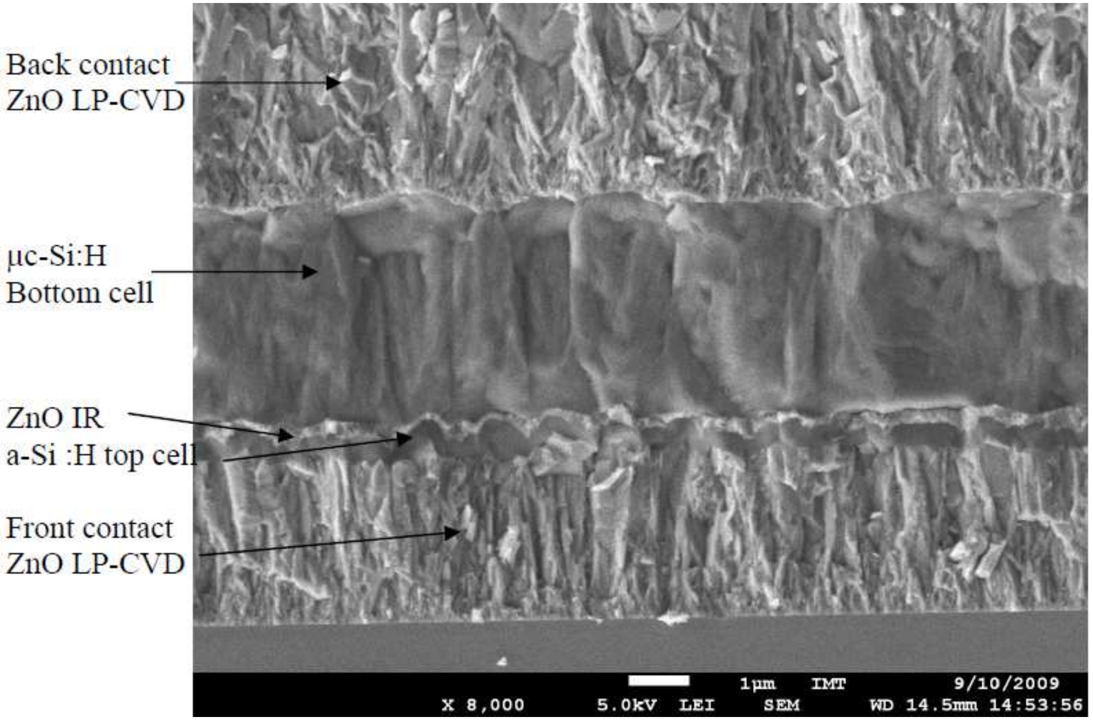
Solar Transparent Conductors?

1. <u>Many</u> solar cells employ at least one ZnO-based layer.

2. ZnO thickness/positioning & form are integral to cell design

3. ZnO represents significant proportion of overall PV structure (& its' cost)…

4. ZnO is multifunctional (electrode, template/buffer & light management: AR & trapping)



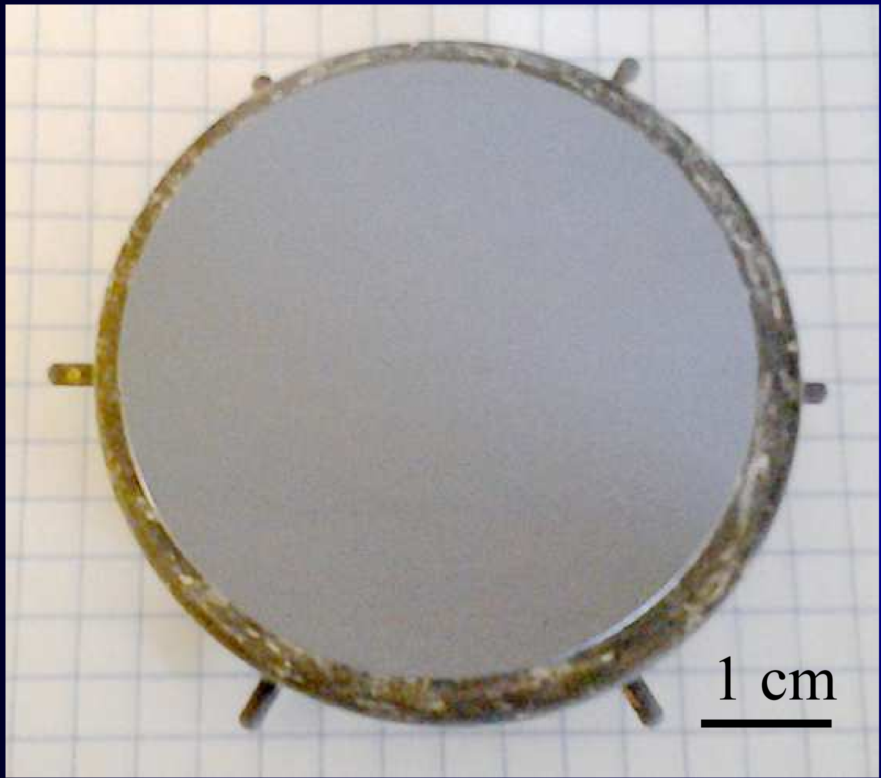
Soderstrom et al. Prog. Photovolt: Res. Appl. (2008)

ZnO-Based Anti-Reflection Coatings

www.greenmybungalow.com

Nano ZnO samples look like « black silicon »

nanovation

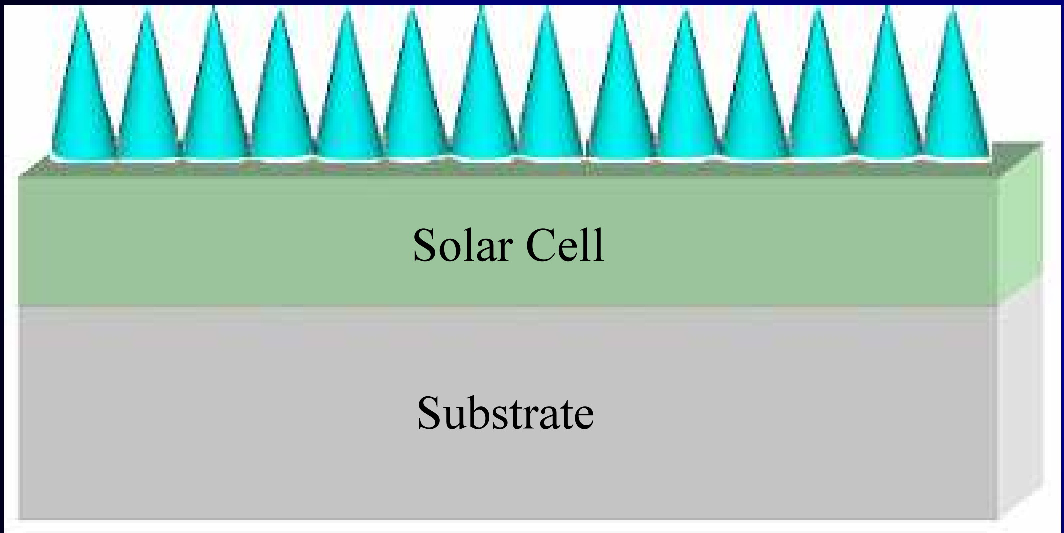


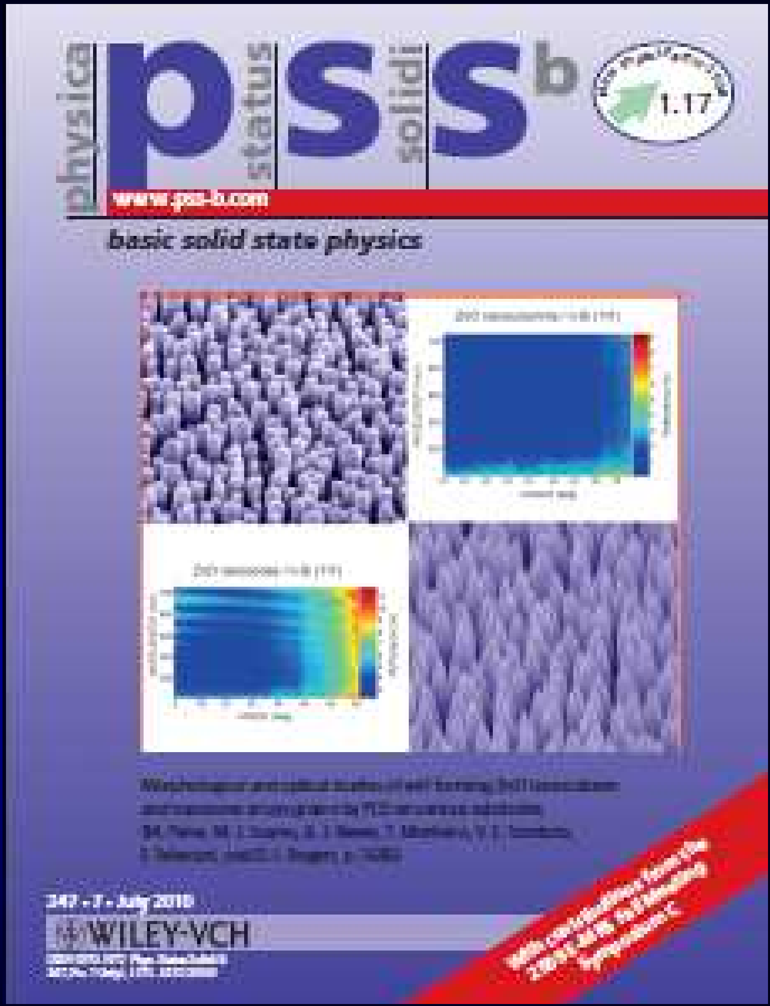
Before Growth

After Nanostructure Growth

Sandana, Rogers et al. Phys. Status Solidi A 211,2 (2014) 449

ZnO Moth-eye Nanostructures as AR Coatings on PV



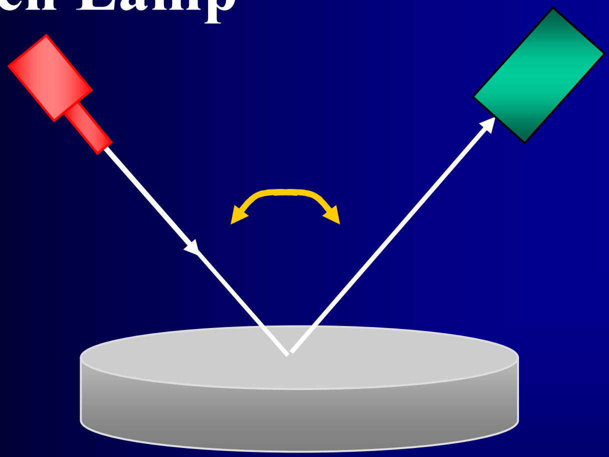


Peres , Rogers et al. Phys. Stat. b, 1–4 (2010) 1695

Reflectivity Measurements

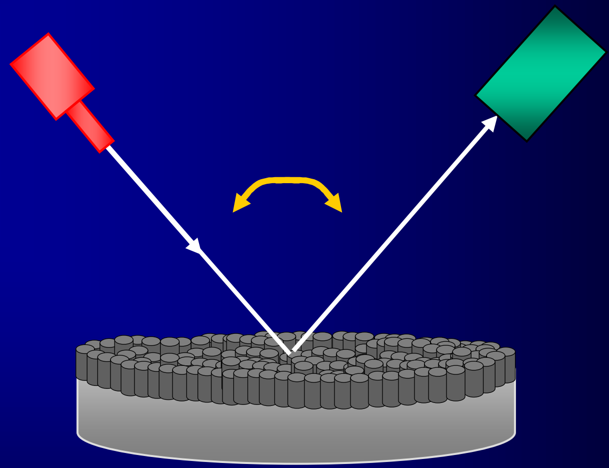
Collimated Tungsten Halogen Lamp

Ocean Optics UBS4000 spectrometer



Bare Si (reference)

Sample Measurement

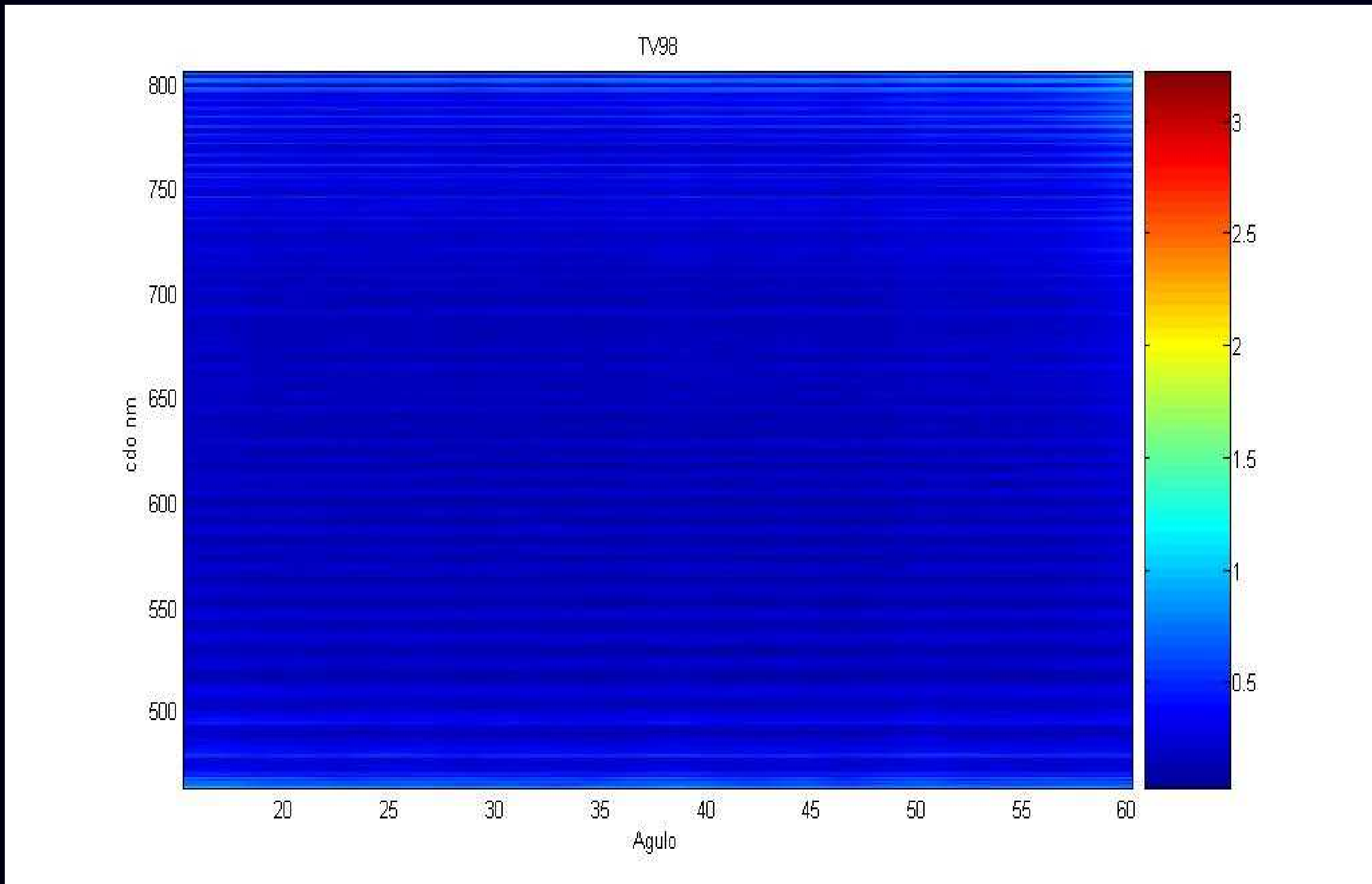


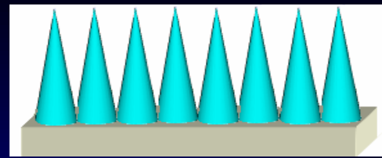
Nanostructures/Si

Peres , Rogers et al. Phys. Stat. b, 1–4 (2010) 1695

Normalised Reflectivity From Nanocones

nanovation





(~ 0.5%) reflection

up to 60º

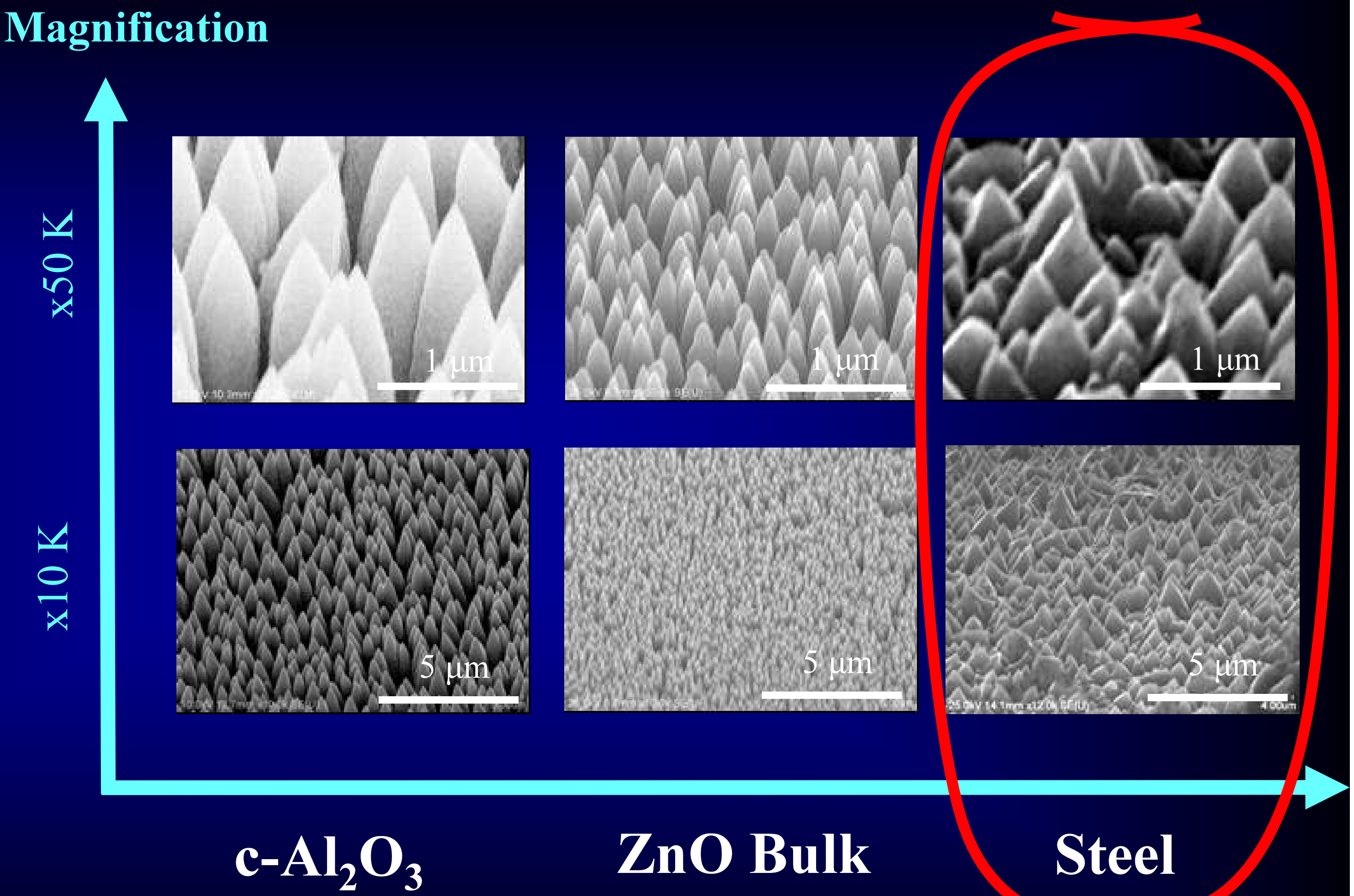
incidence

- omni-directional "moth eye" AR behaviour for whole visible spectrum

Peres , Rogers et al. Phys. Stat. b, 1–4 (2010) 1695

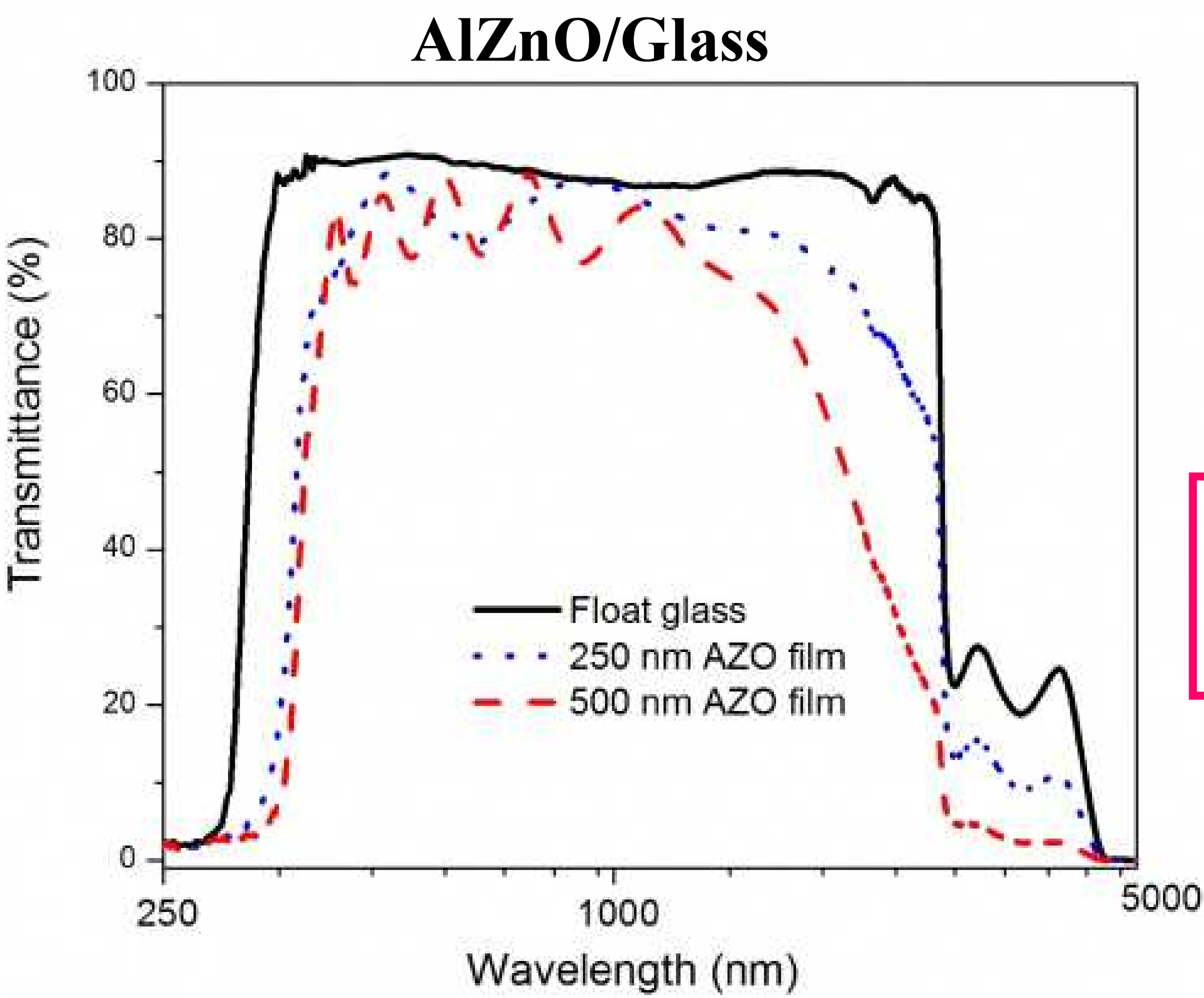
PLD Nano ZnO on Various Substrates

nanovation



Sandana, Rogers et al. Phys. Stat. Solidi C, 10 (2013) 1317

Good NIR & MIR Transmittance…

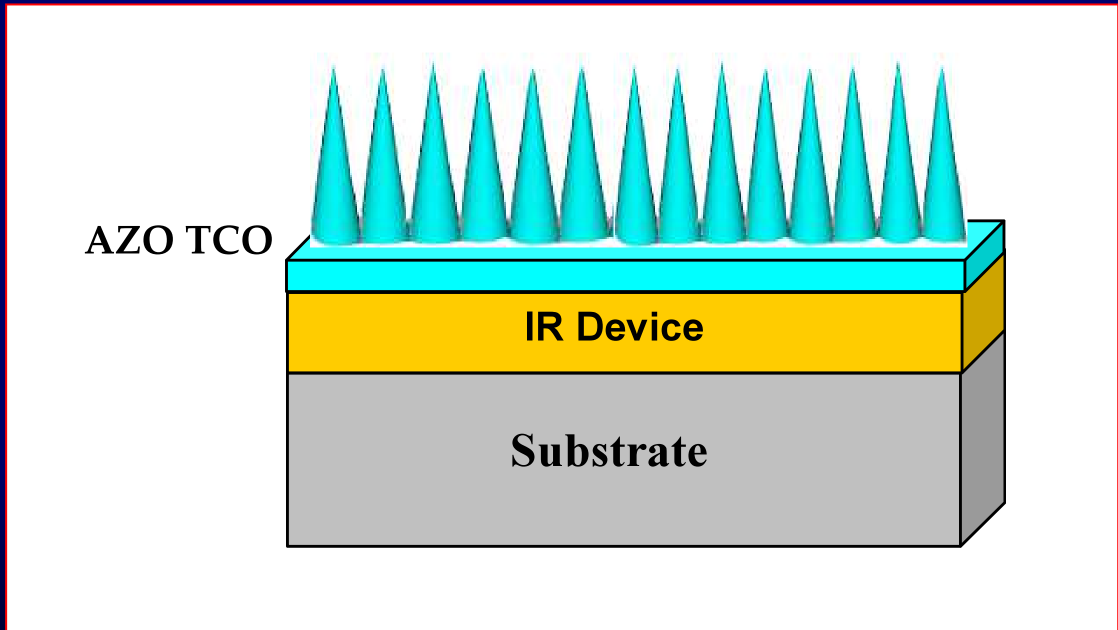


sheet resistance ~ 25 Ω/□

$n_C \sim 2.4 \times 10^{20}$ cm−3

Dhakal et al. Solar Energy (2012)

ZnO Moth-eye Nanostructures as Anti-Reflective Contacts on IR Devices



3. ZnO Piezogenerators

Selecting Piezoelectric Materials

Material	Formula	Form	Piezoelectric constant (pm/V or pC/N)
Ammonium dihydrogen phosphate (ADP)	$NH_4H_2PO_4$	Single crystal	$d_{36} = 48$
Barium titanate	$BaTiO_3$	Single crystal	$d_{15} = 587$
Barium titanate	$BaTiO_3$	Polycrystalline ceramic	$d_{15} = 270$
Lead zirconate titanate (PZT)	$PbZr_{0.6}\,Ti_{0.40}O_3$	Polycrystalline ceramic	$d_{33} = 117$
Lead lanthanum zirconate titanate (PLZT)	$Pb_{0.925}La_{0.5}Zr_{0.56}Ti_{0.44}O_3$	Polycrystalline ceramic	$d_{33} = 545$
Polyvinylidene fluoride	$(CH_2CF_2)_n$	Oriented film	$d_{31} = 28$
Potassium dihydrogen phosphate (KDP)	KH_2PO_4	Single crystal	$d_{36} = 21$
Quartz	SiO_2	Single crystal	$d_{11} = 2.3$
Zinc oxide	ZnO	Single crystal	$d_{33} = 12$

Why ZnO?

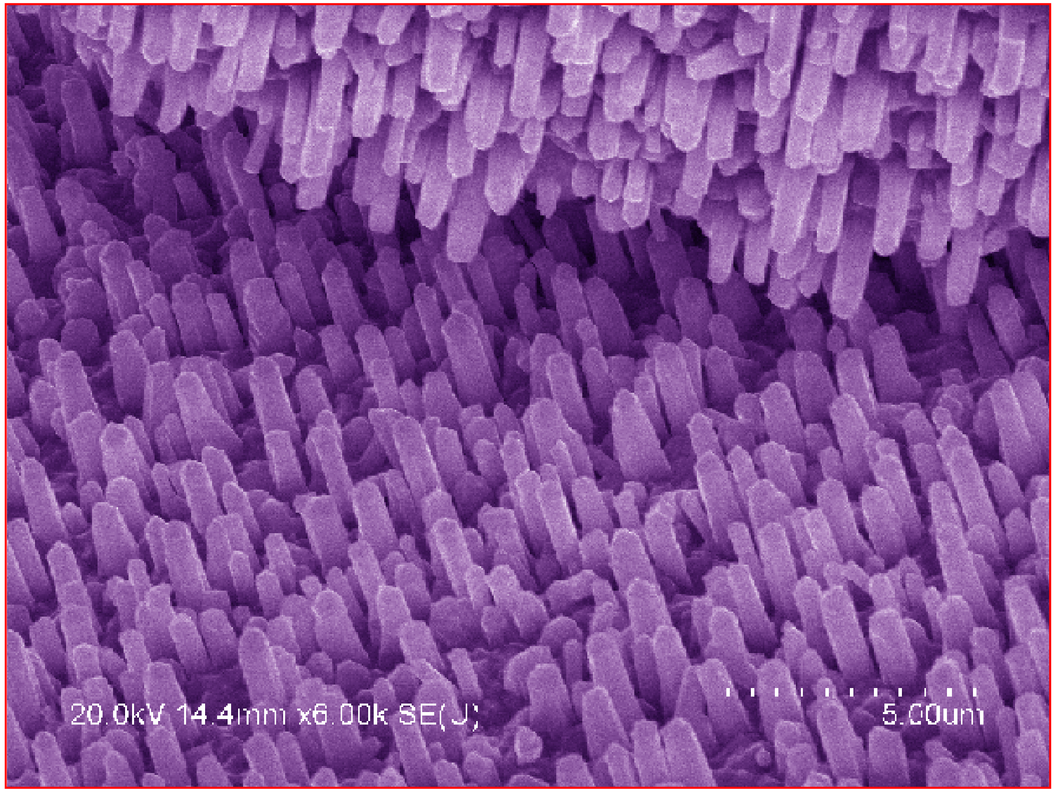
Robust/Malleable

Cheap & no poling required

Easy to make/nanostructure

Biocompatible

High temperature resistant

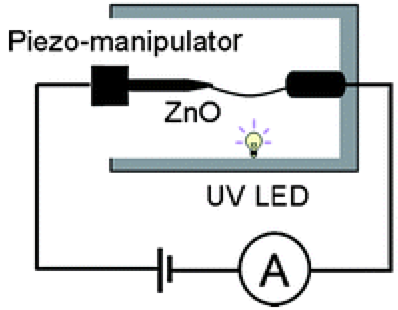


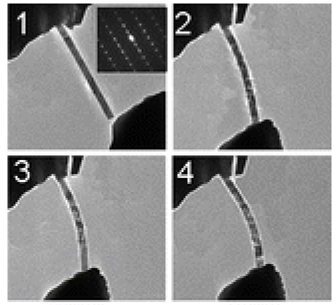
Integrating with multifunctional possibilities of ZnO

Rogers et al. Laser Focus World 49, 10 October (2013)

Nanowire elasticity

➔ Broad frequency response: few Hz to MHz





Gao et al. J. Mater. Chem. 7, 2009

Potential for enhanced piezo response

Piezoelectric coefficient d_{33} in nanostructured materials compared to bulk.

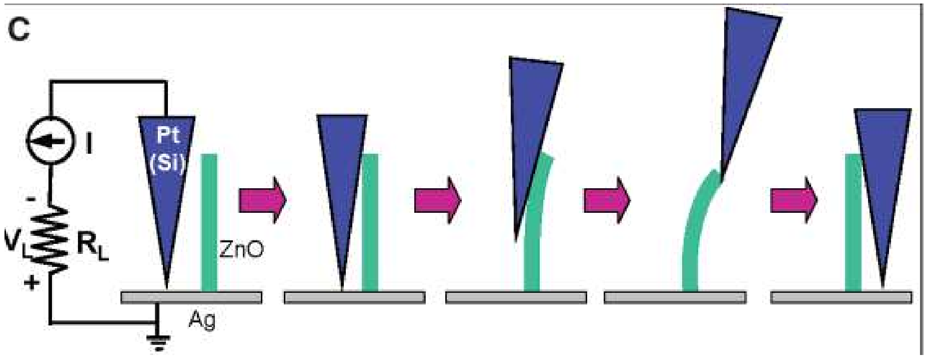
Material	d_{33} (pm/V)		
	Theoretical (nanoscale)	Experimental (nanoscale)	Experimental (bulk)
PVDF		–38[10]	–25
PZT		101[9]	650
ZnO	168.2[8]	14–26.7[7]	9.93
GaN	65.8[8]	12.8[28]	1.86
PMN-PT	N/A	381[13]	2,500[29]

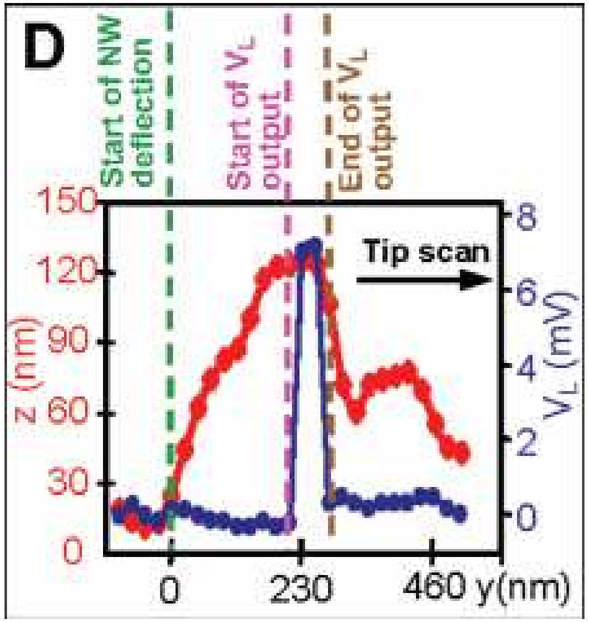
Conducting

Can harvest tiny motions

Ardilla et al. Future Trends in Microelectronics (2013) 230

2006: ZnO Vertical NW Generators with AFM





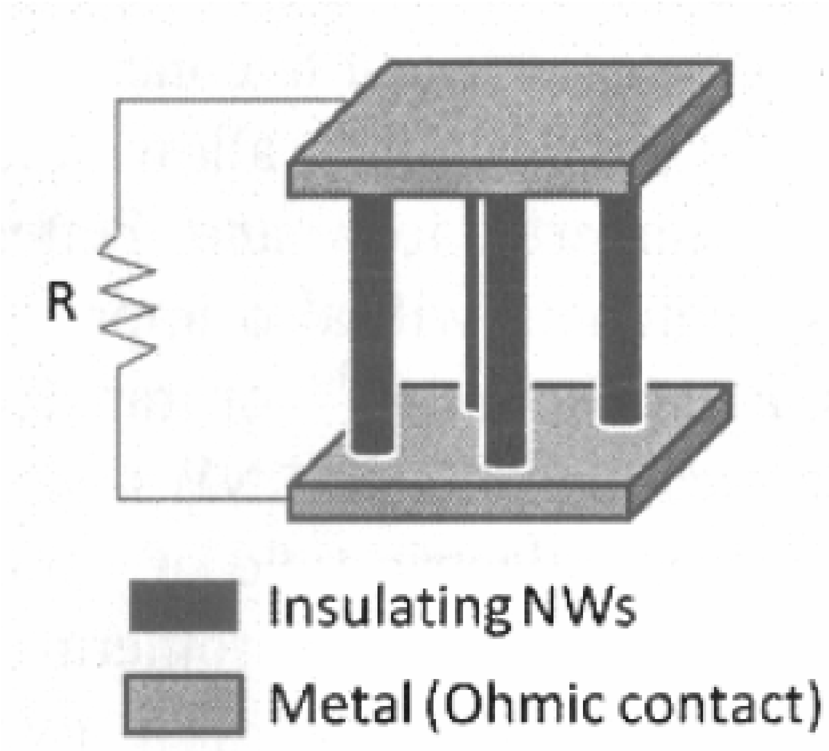
Requires 1 Schottky & 1 Ohmic contact

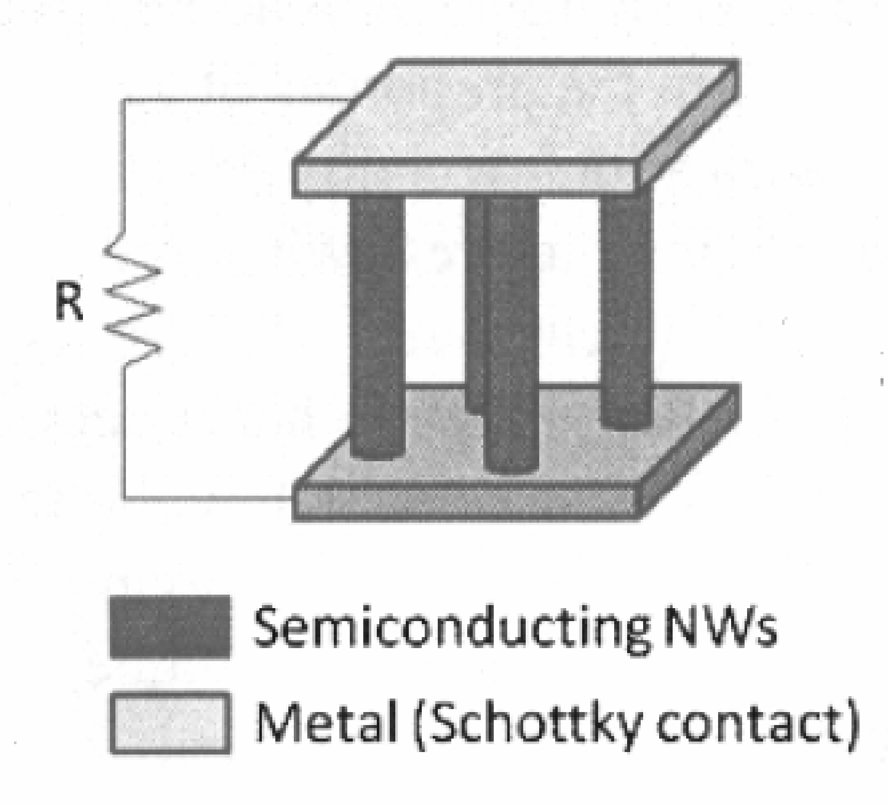
Very small signal: ~ 16 pA

Z.-L. Wang & J. Song

Piezoelectric Nanogenerators Based on ZnO NW Arrays, Science, vol 312, pg 242-45 (2006)

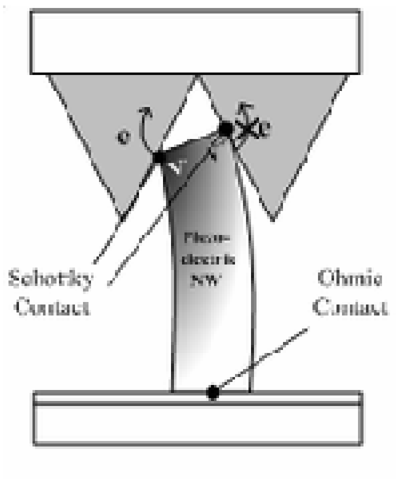
Contacts…



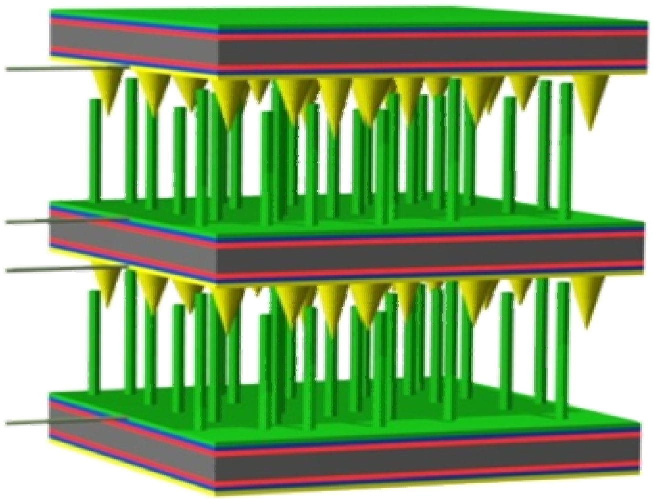


Ardilla et al. Future Trends in Microelectronics (2013) 230

Harvesting energy from many nanowires



Parallel contacting increases current

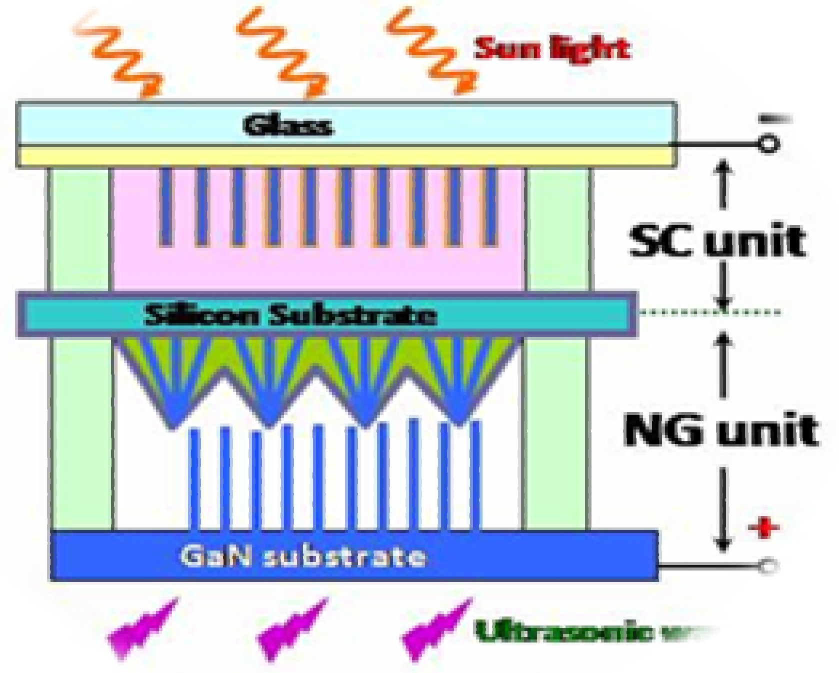


Series stacking increases voltage

Wang et al.
***Science,** 312 (2006) 242.*
***Science** 316 (2007) 102*
***Nature** 451 (2008) 809*
***Nature Nanotech.**, 4 (2009) 34*

Demonstration…

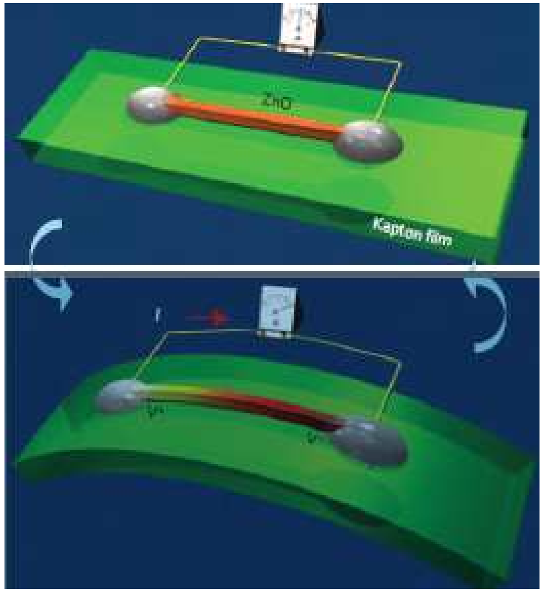
Hybrid solar/piezo cell

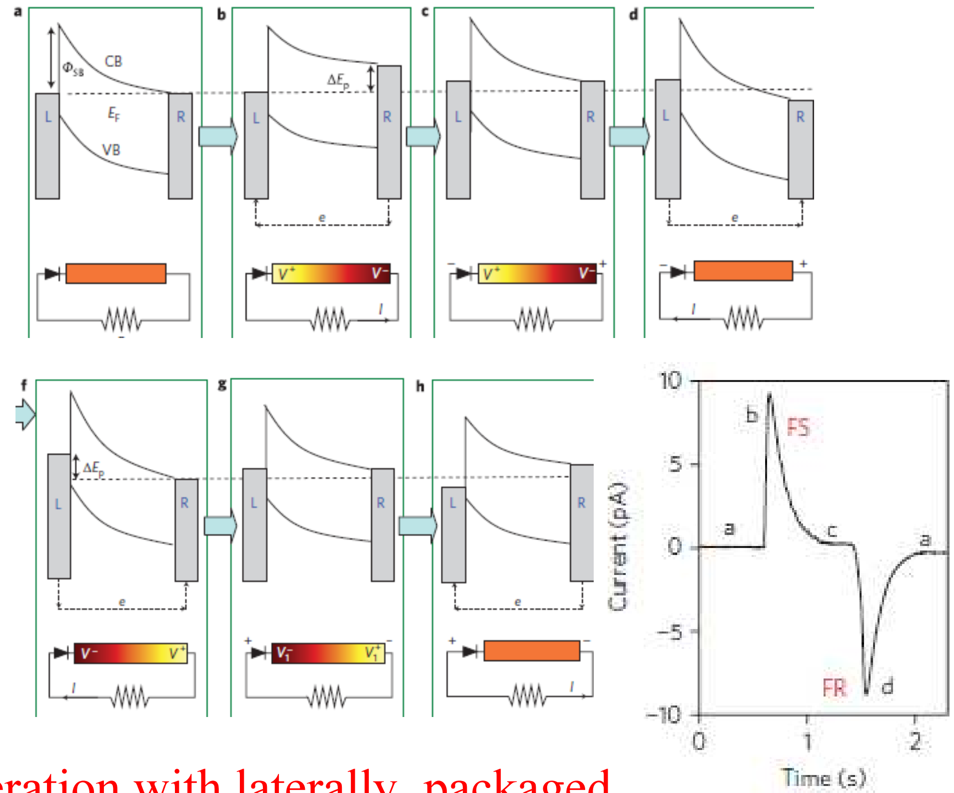


Wang et al. JACS, *131* (2009) 5866

ZnO Piezogenerators Background: Nano → Micro

2008: ZnO Lateral Single Wire Generators





Simpler construction
Simpler measurement
Larger signal

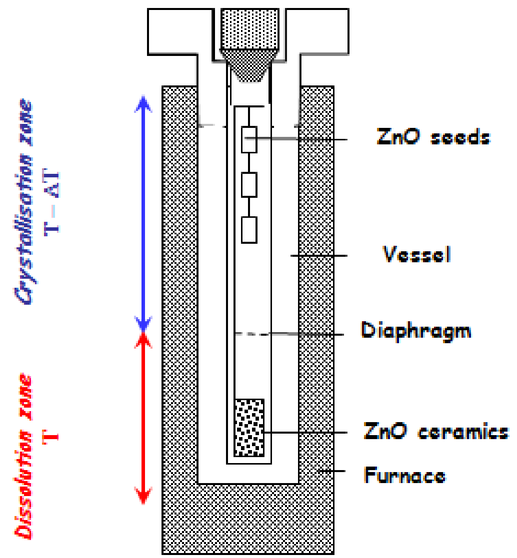
R. Yang et al. Power generation with laterally packaged piezoelectric fine wires, Nature Nanotechnology 4 (2009)

Nanovation/Bordeaux ZnO Piezogenerators

nanovation

Idea: bigger crystals ➔ superior robustness & signal + better contacts

Hydrothermal Autoclave



On the bottom: Dissolution of the nutrient (ZnO as powder or ceramics) by the solvent KOH
On the top: Deposition of ZnO in solution on the seeds
Role of ΔT : Transfer of matter from the top to the bottom: kinetic

CONDITIONS

Seed: ZnO compacted 6000 bar, 15mn

Compression 300°C (3h)

KOH 3 mol/l + O_2 65 bar,

T = 350 °C +/- 10°C,

1600 bar for 6.5 days

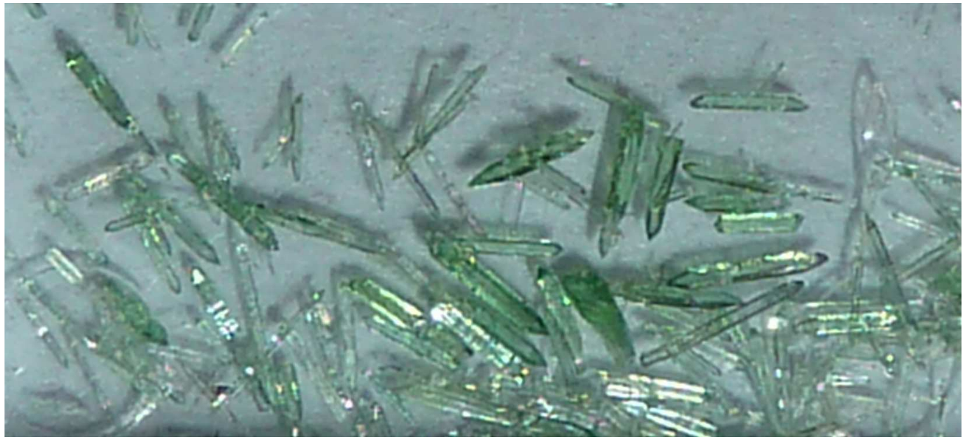
icmcb

cnrs

nanovation

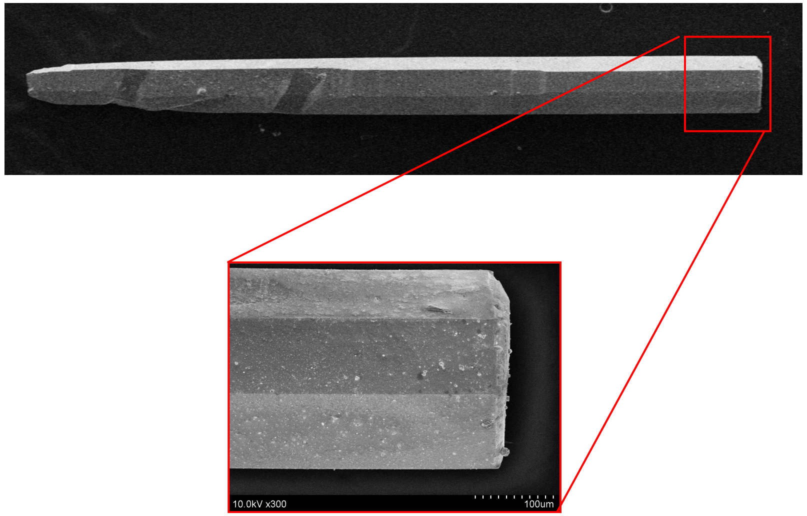
Rogers et al. Proc. SPIE 8263 (2012) 82631X-1

U. Bordeaux ZnO Micro-crystals



1 mm

Scanning Electron Microscopy

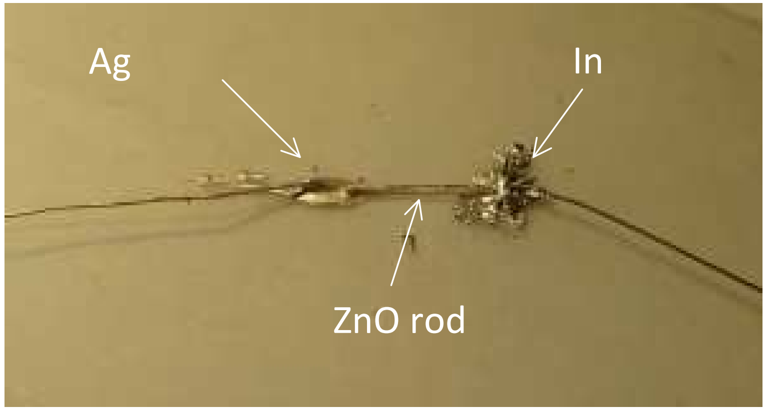


Faceting suggests single crystal nature

Rogers et al. Proc. SPIE 8263 (2012) 82631X-1

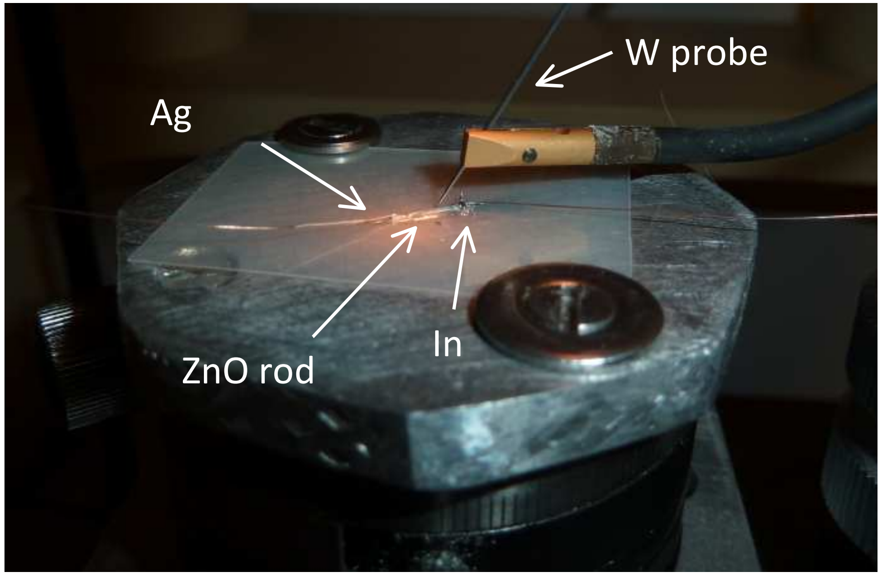
Nanovation/Bordeaux ZnO Piezogenerators

Ag (Schottky) & In (Ohmic) Contacts on Teonex Support



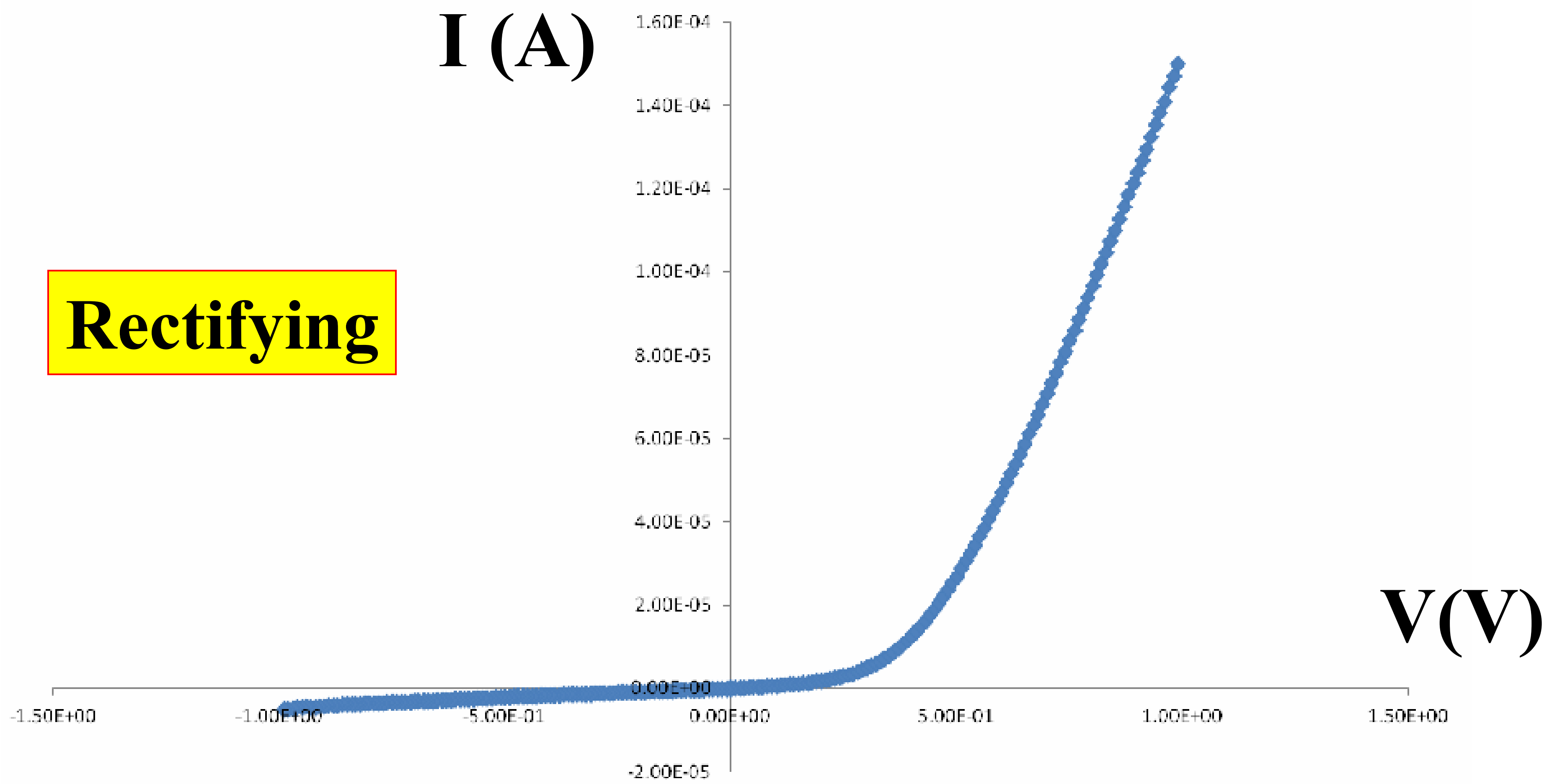
1 mm

Bending with Probe Arm



Rogers et al. Proc. SPIE 8263 (2012) 82631X-1

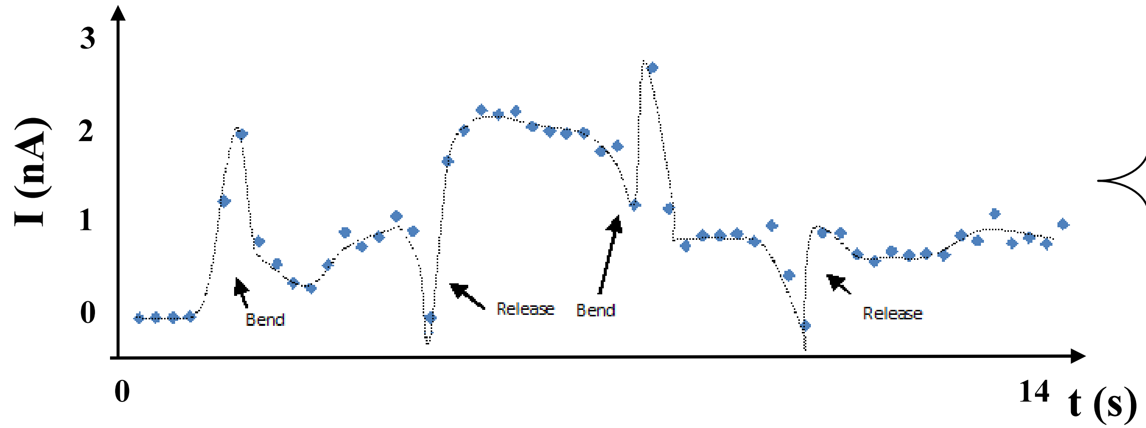
I/V Characteristic…



Rogers et al. Proc. SPIE 8263 (2012) 82631X-1

I & V as a function of time…

nanovation

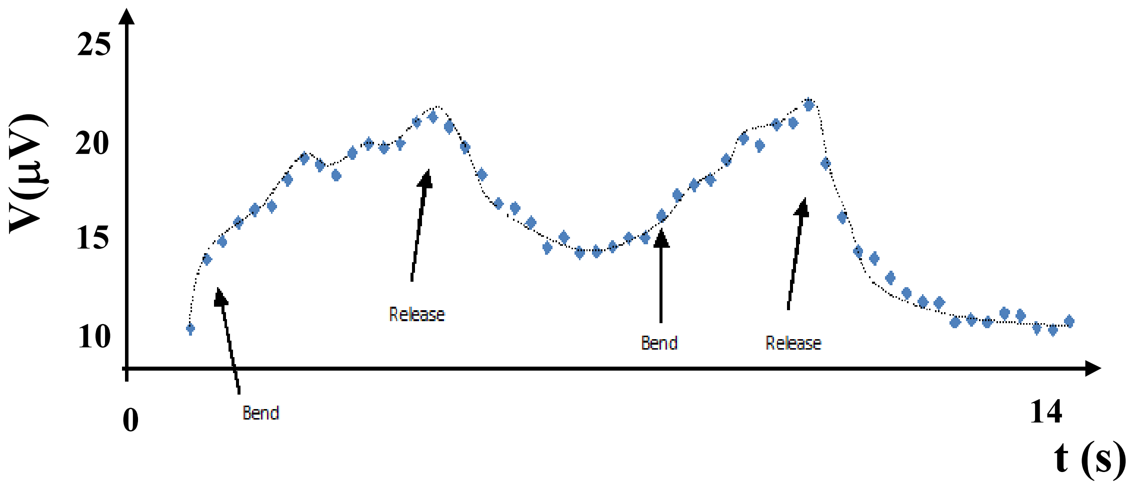


Stress ➔ piezopotential field

➔ charges accumulate on electrodes (like dipole moments in capacitor)

release ➔ piezopotential disappears

➔ back flow of electrons.



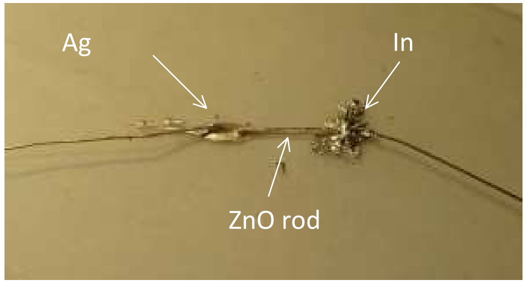
resembles capacitor charge/discharge

~ 2 nA
~ 10 µV

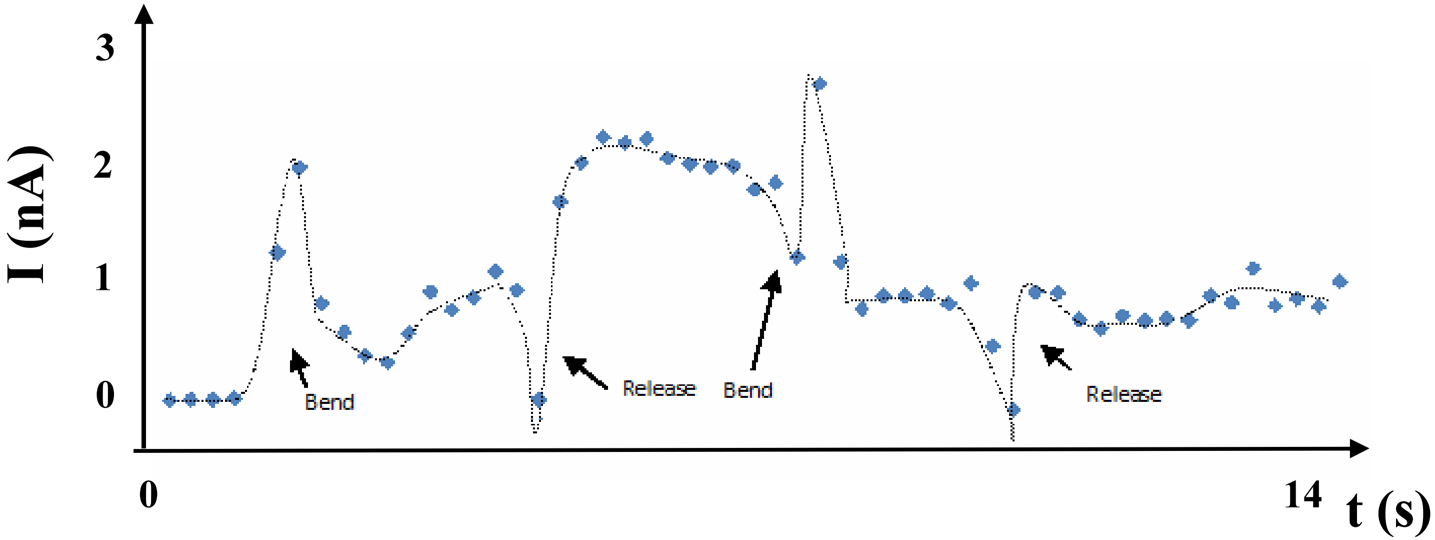
Rogers et al. Proc. SPIE 8263 (2012) 82631X-1

Control Experiment…inert rod

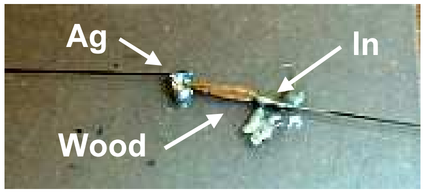
ZnO rod



1 mm



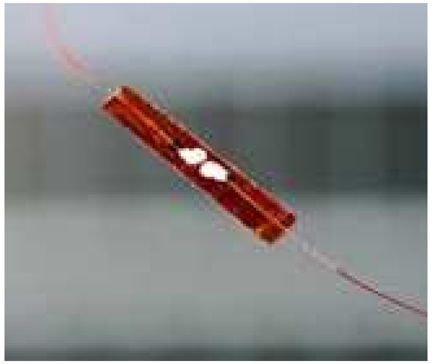
Wooden rod

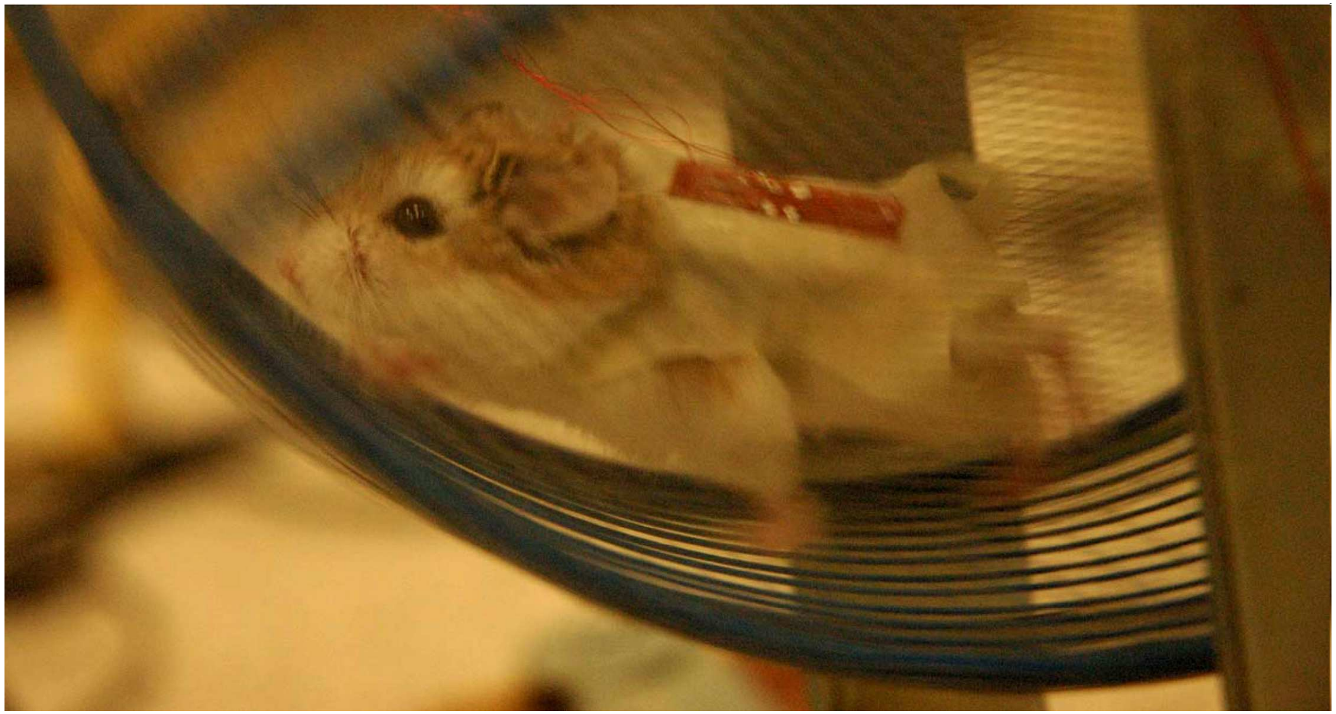


Rogers et al. Proc. SPIE 8263 (2012) 82631X-1

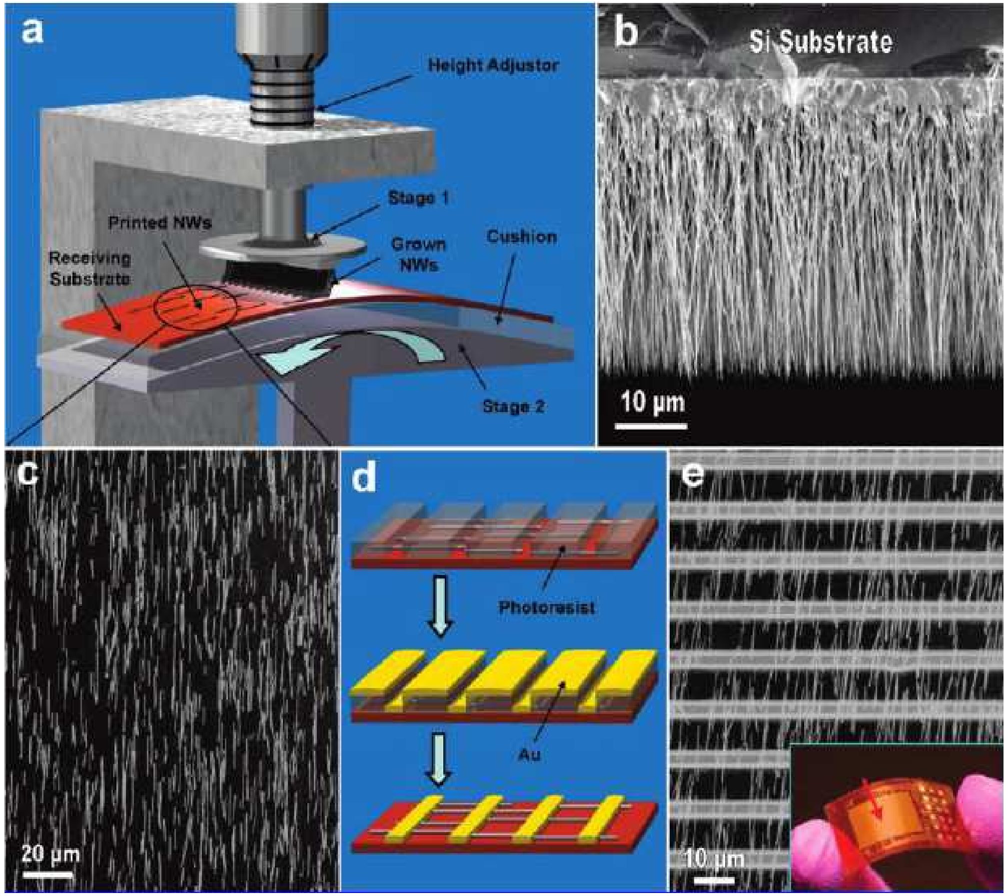
Single Wire Generator demonstration…

$\leq$ 5 x 300 μm





Flexible High Output Nano generator (HONG)



V ~ 2.03 V

I ~ 107 nA

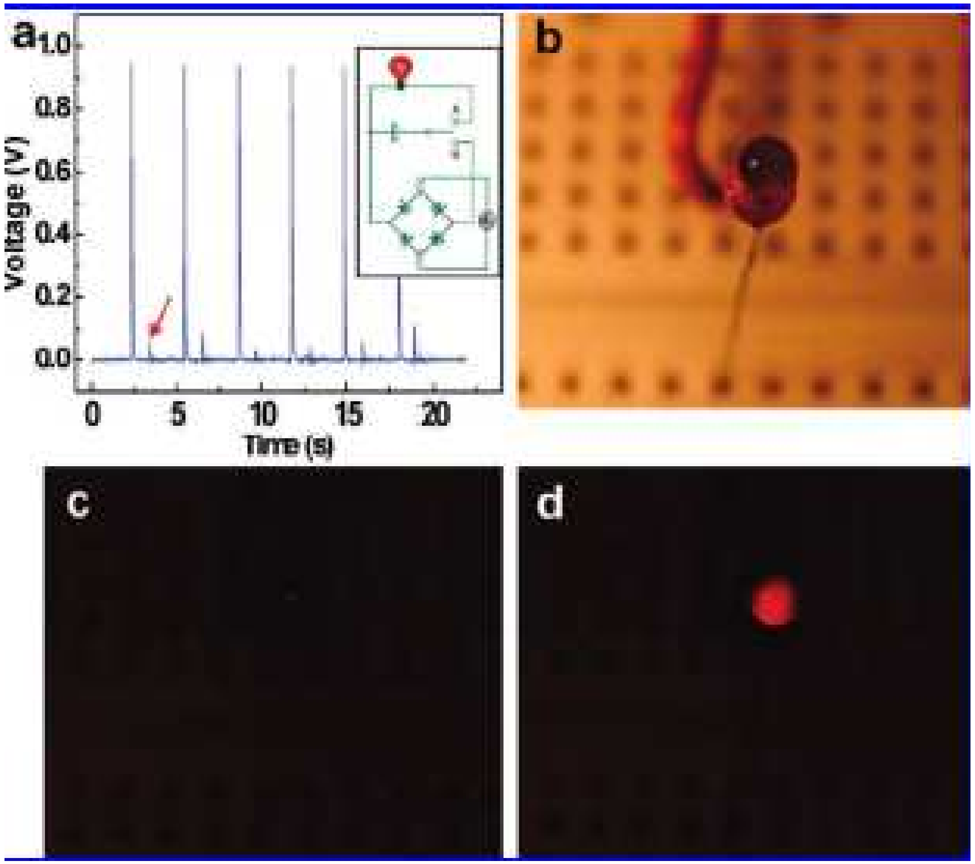
efficiency ~ 4.6%

power density ~11 mW/cm^3,

i.e. 22x PZT cantilever signal.

Zhu et al. Nanoletters (2010)

Piezogenerator-powered LED

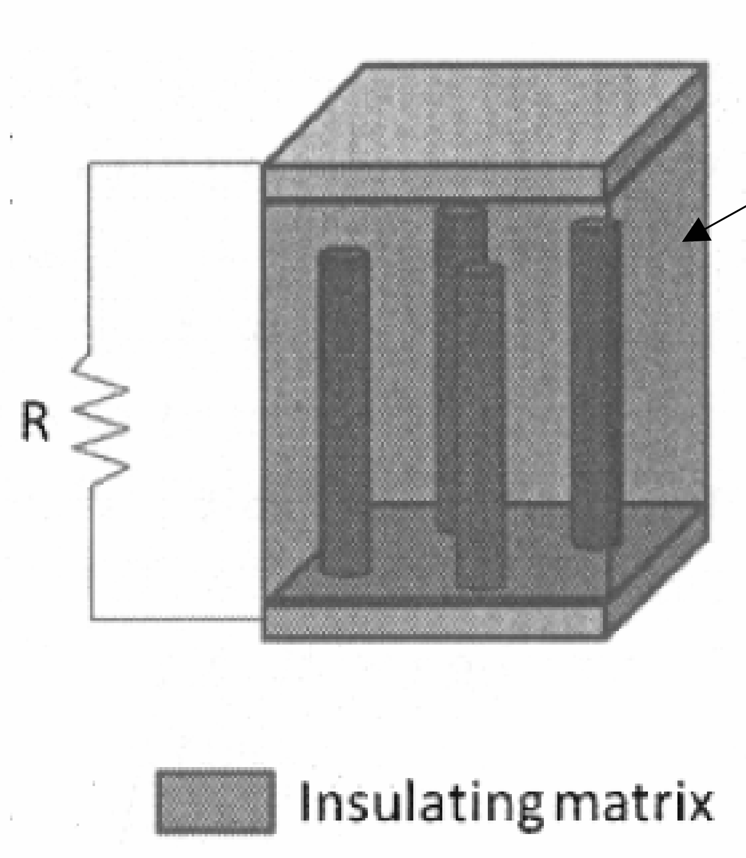


Zhu et al. Nanoletters (2010)

Also:

- **mobile electronics**
- **defense technology**
- **clothing**
- **flags**
- **building decorations**
- **shoes**
- **self-powering sensors**
  - **cargo shipping tracking system**
  - **environmental inspection**
  - **infrastructure monitoring**
  - **health monitoring/body implants (e.g. glucose/blood pressure sensors)**

Contacts…



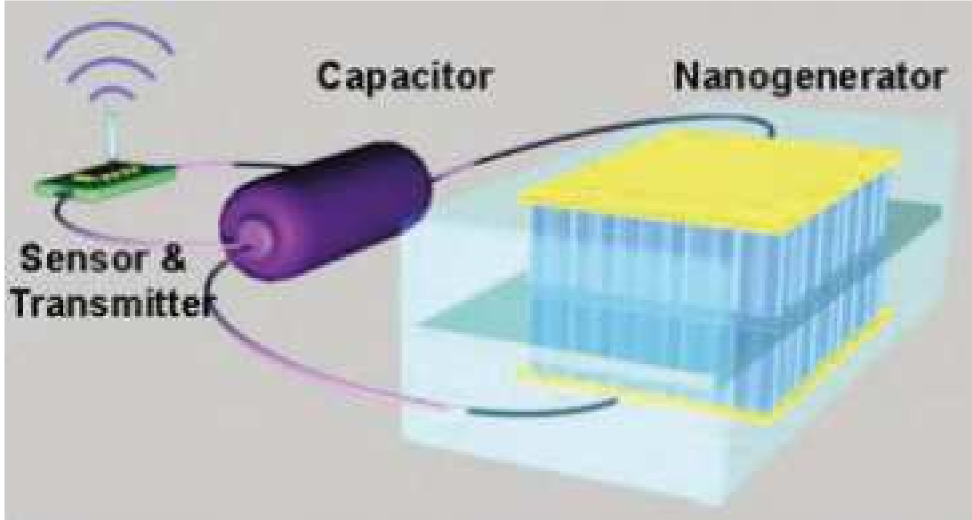
Typically PMMA or a p-type polymer

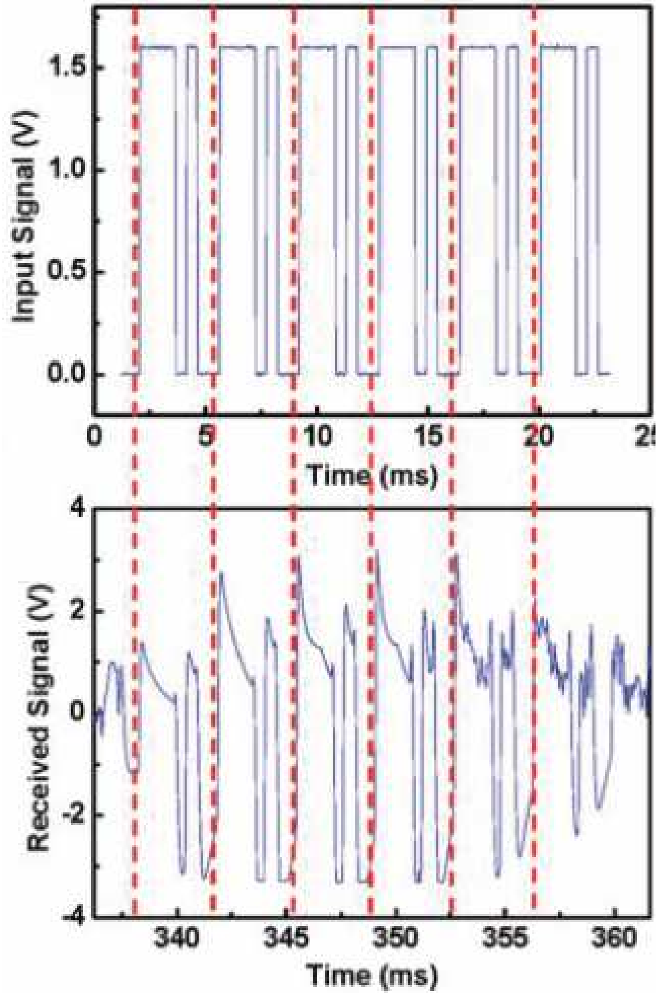
ADVANTAGES

- Infinite potential barrier (prevents e^- flow through ZnO)
- Easier contacting
- All nanostructures leveraged (irrespective of height)
- Improved robustness/durability

Ardilla et al. Future Trends in Microelectronics (2013) 230

Self-Powered Wireless Data Transmission

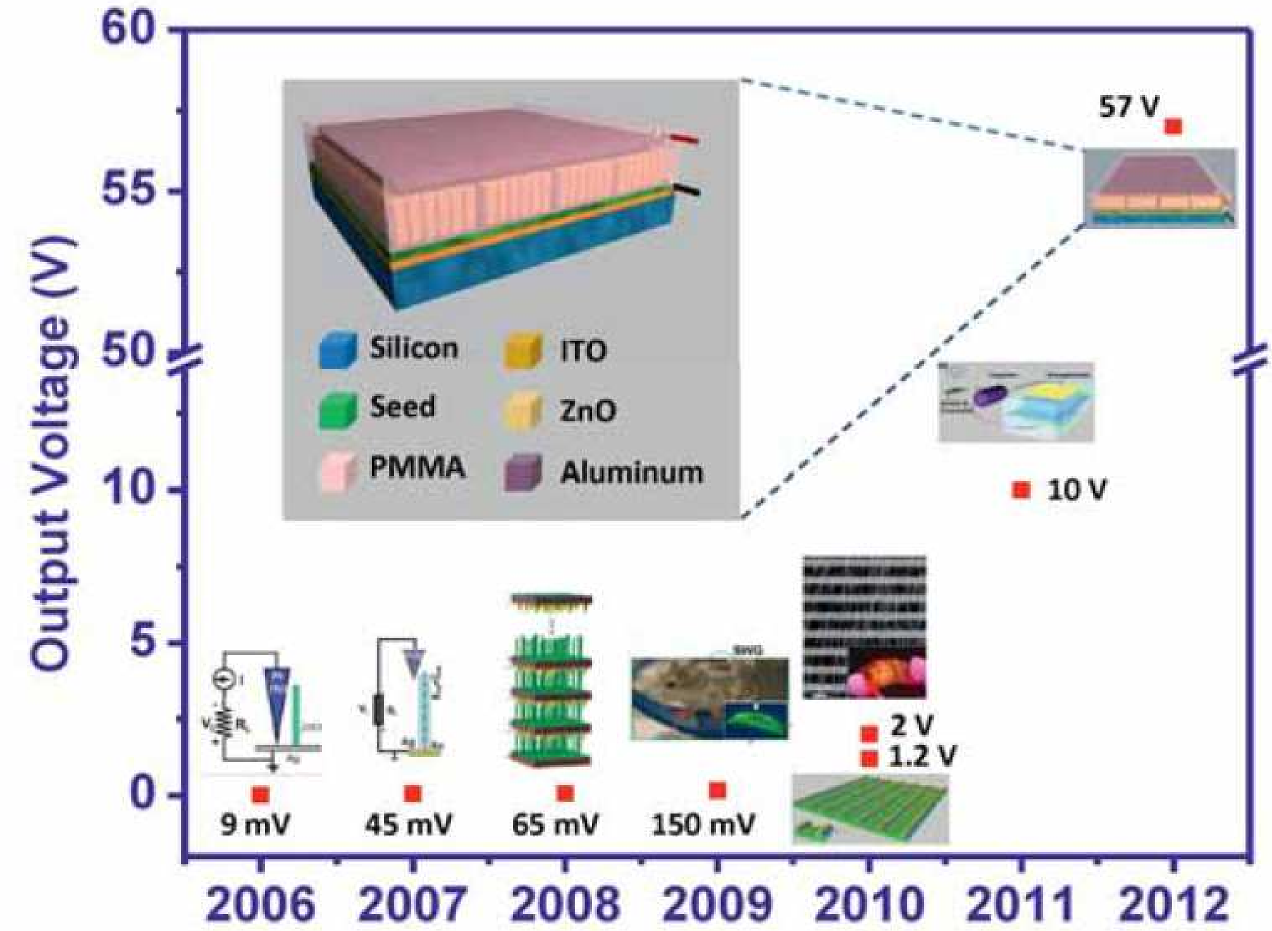




Hu et al. Nanoletters (2011)

Power density = 10mW/cm^3

Development of ZnO nanogenerator output



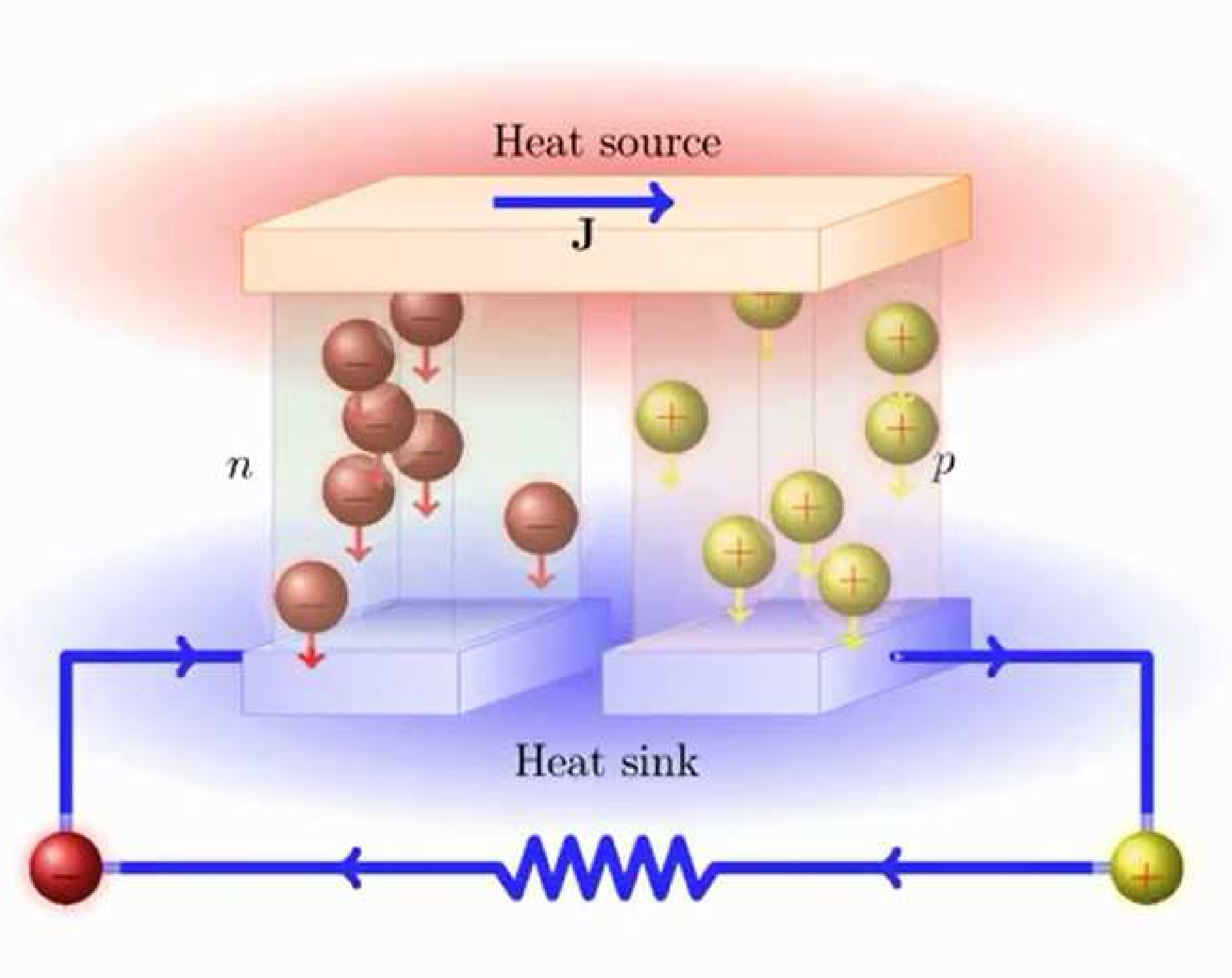
Inset: schematic of most recently developed nanogenerator with aligned ZnO arrays.

V_{OC} = 57 V
I_{SC} = 12 μA
(~ 1cm^2)

Z. L. Wang et al. Materials Today (2012)

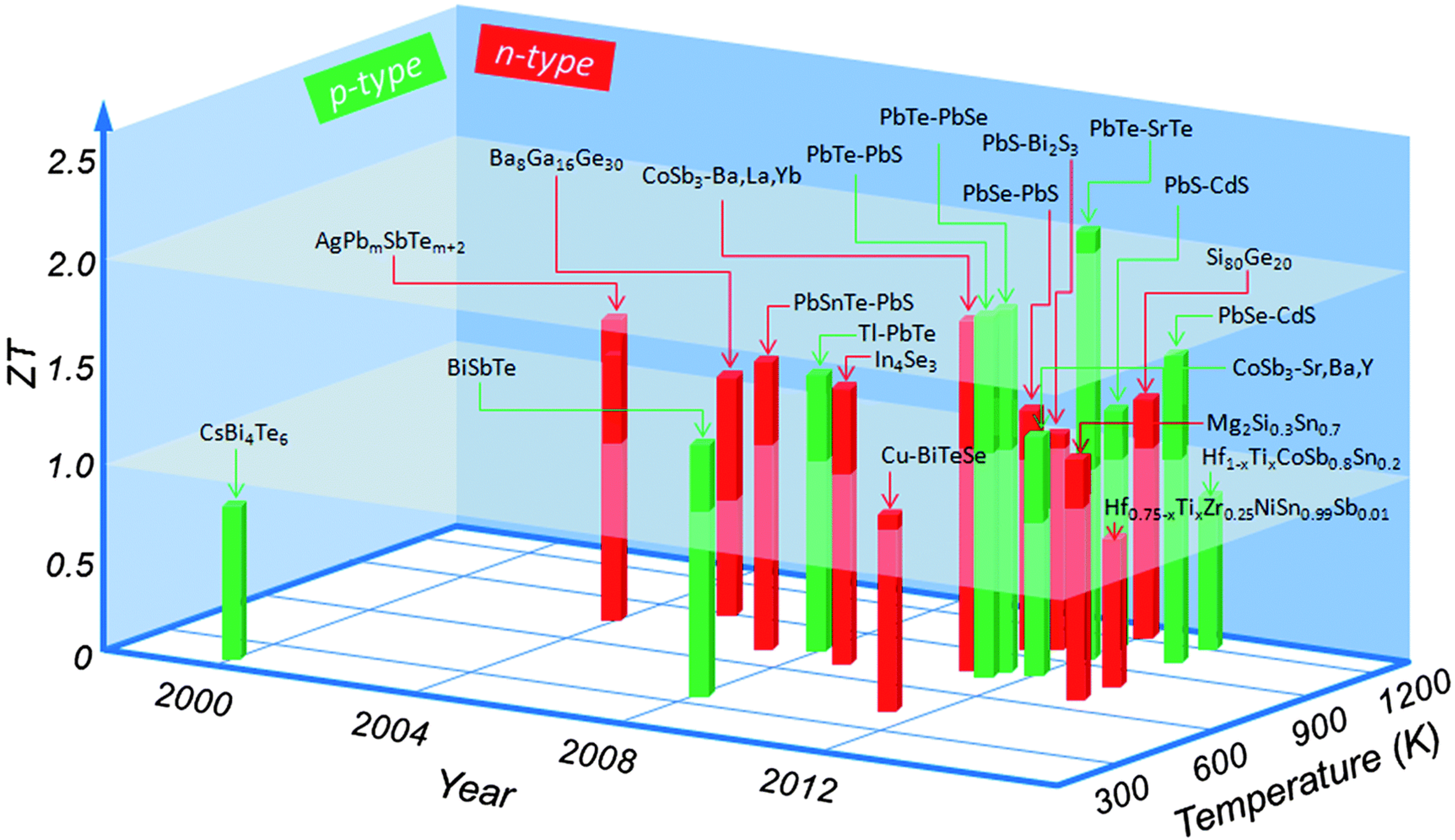
4. ZnO-based Thermoelectrics

Thermoelectrics Dilemma



Need
- heat source & heat sink
- p-type material
- n-type material
- large thermal gradient
- good electrical conductivity

State-of-the-Art Bulk Thermoelectric Materials



L-D Zhao et al. Energy Environ. Sci., 2014, 7, 251

Drawbacks with Current Thermoelectrics

nanovation

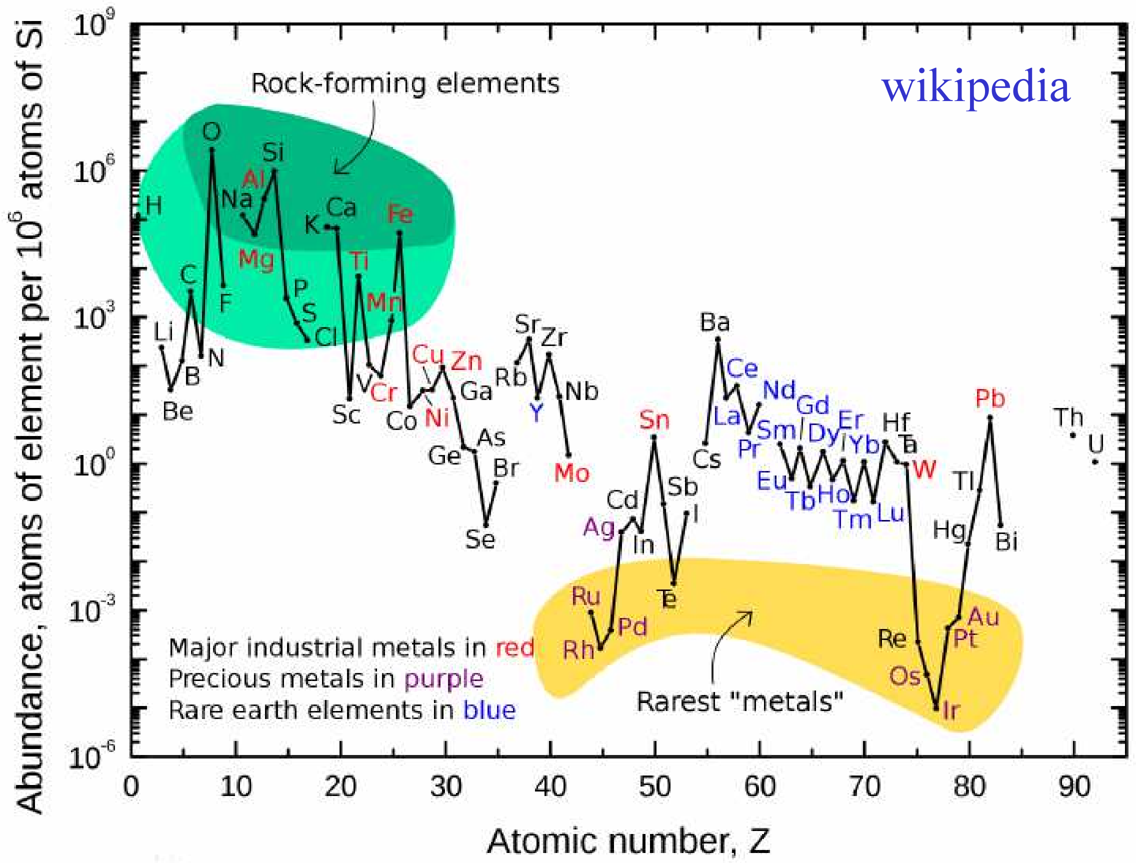
KT Too Low

Rarity of Te

Toxicity of Te

Low Melting Points:

(585°C for Bi_2Te_3)



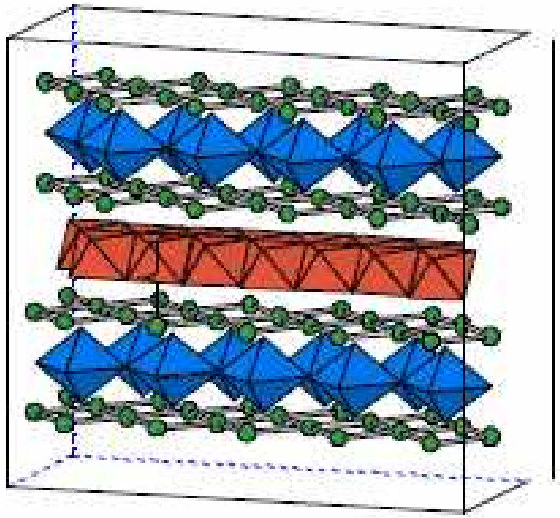
Why Oxide Thermoelectrics?

Price, toxicity & stability in air are key drivers…

State-of-the-art p-type oxides are layered cobalites:

e.g. $Ca_3Co_4O_{9-\delta}$

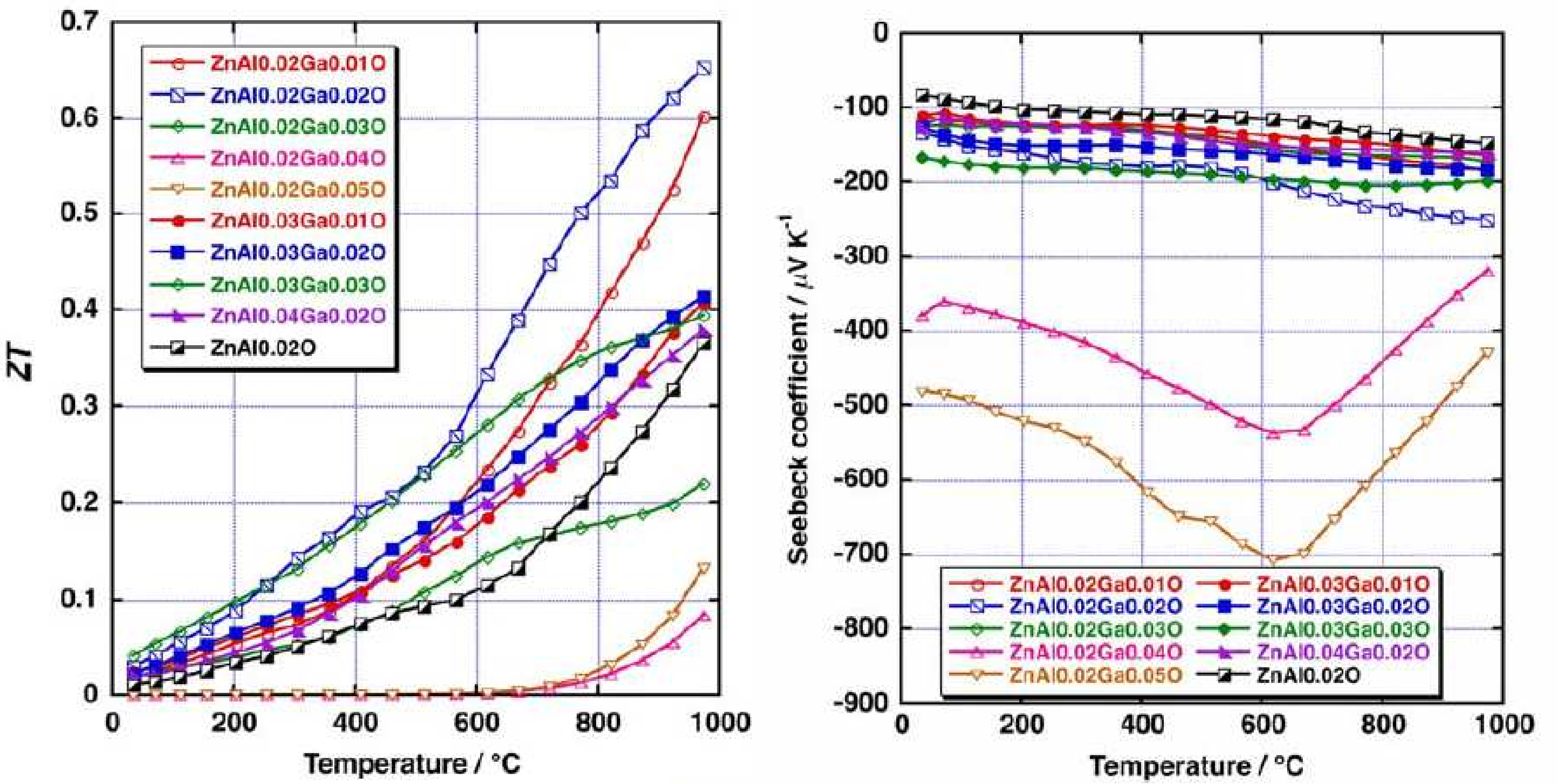
ZT = 0.65 at 1247K



(Al, Ga)ZnO: highest n-type oxide ZT…

nanovation

High Thermoelectric Performance of Dually Doped ZnO Ceramics

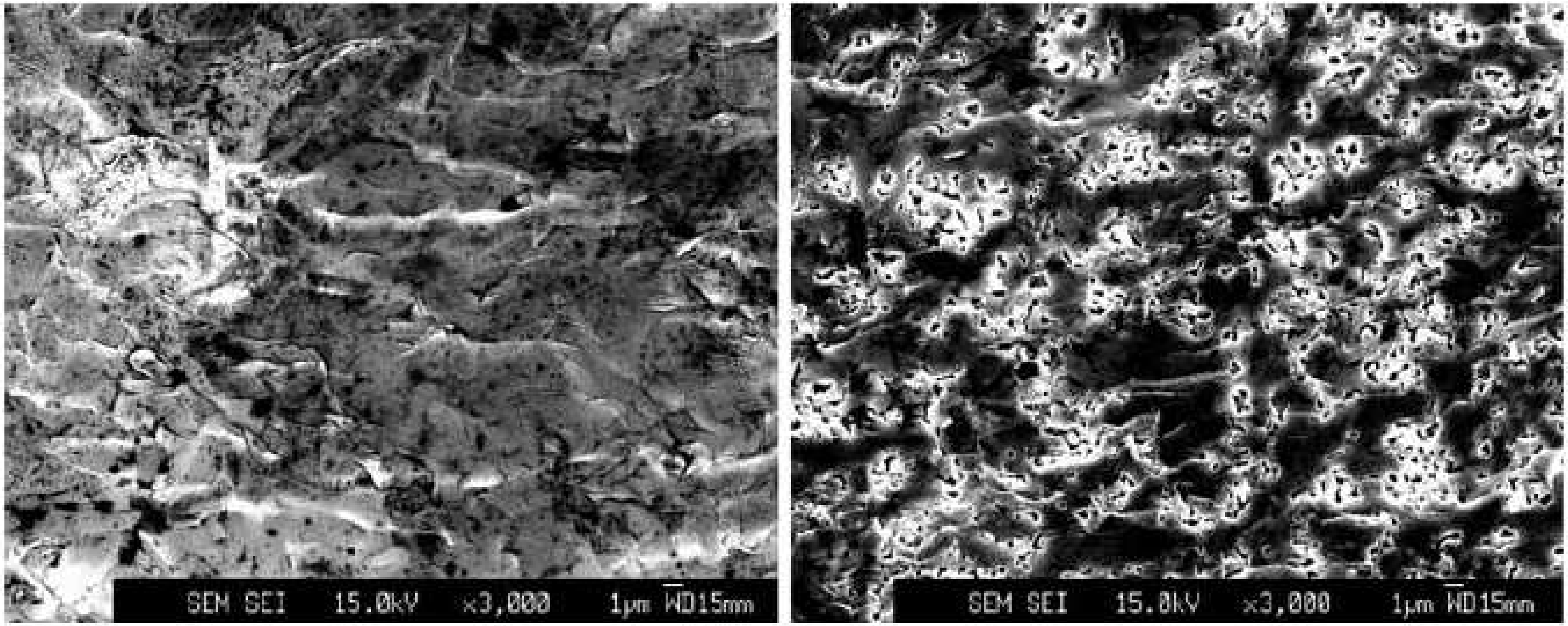


Ohtaki et al. Journal of ELECTRONIC MATERIALS, Vol. 38, No. 7, 2009

(Al, Ga)ZnO: highest n-type oxide ZT… *nanovation*

High Thermoelectric Performance of Dually Doped ZnO Ceramics

Bulk nanocomposite (Al, Ga)ZnO



SEM images of fracture surfaces of $Zn_{1-x-y}Al_xGa_yO$ (left, $x = 0.02$, $y = 0.02$; right, $x = 0.02$, $y = 0.05$) ceramics.

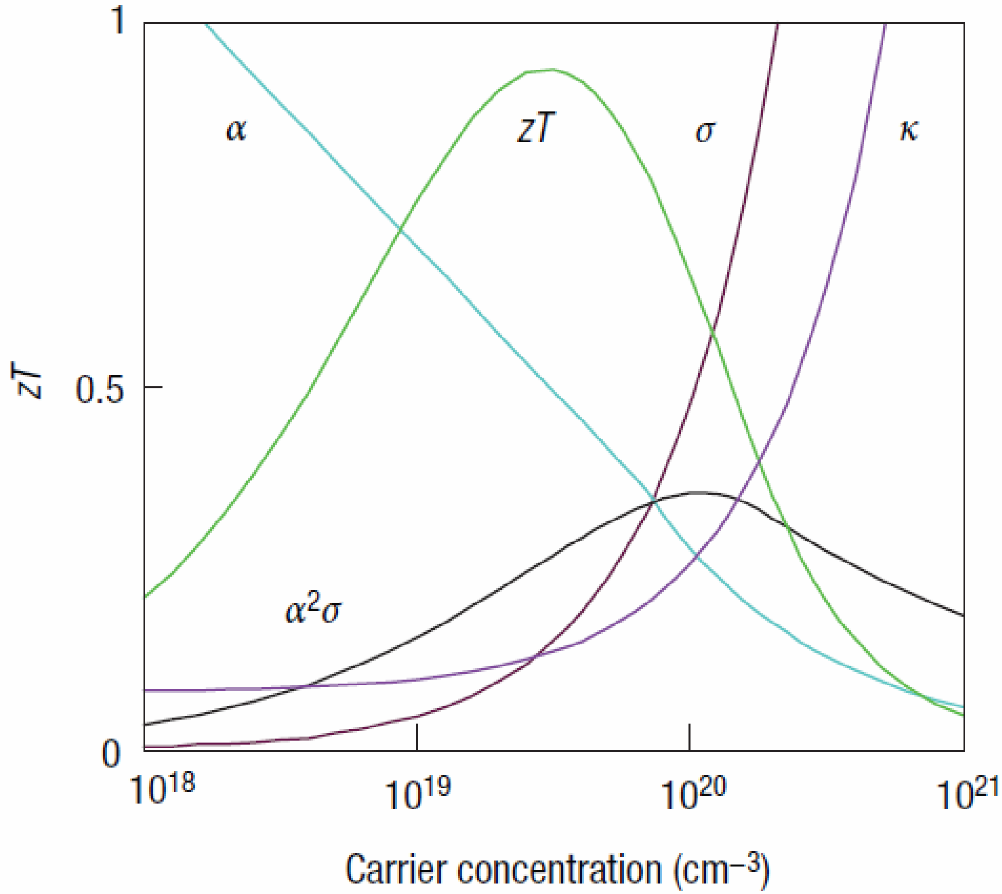
Ohtaki et al. Journal of ELECTRONIC MATERIALS, Vol. 38, No. 7, 2009

Want high ZT
(thermoelectric figure of merit)…

$$\mathbf{ZT} = \frac{\alpha^{\mathbf{2}}\sigma}{\kappa}\mathbf{T}$$

SEEK:
high Seebeck coefficient (α)
high electrical conductivity (σ)
& low thermal conductivity (κ)

Trade-off in order to maximise KT



G. Snyder & E. Toberer, Nature Materials, 7 (2008)

Low Dimensional Structures

- Use of transport along superlattice quantum wells
- Higher α from the higher density of states
- Higher electron mobility in quantum well –> higher σ
- Lower κ_{ph} through additional phonon scattering from heterointerfaces
- Disadvantage: higher κ_{el} with higher σ (but layered structure can reduce this effect)
- Overall Z and ZT should increase

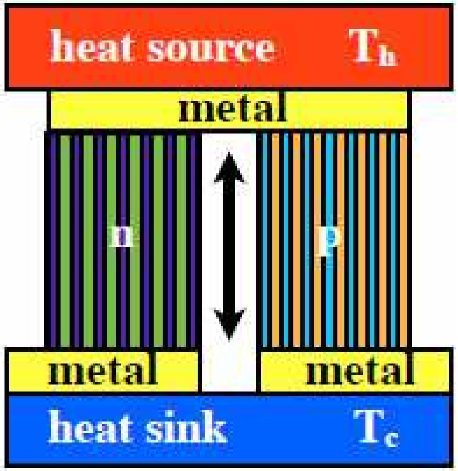
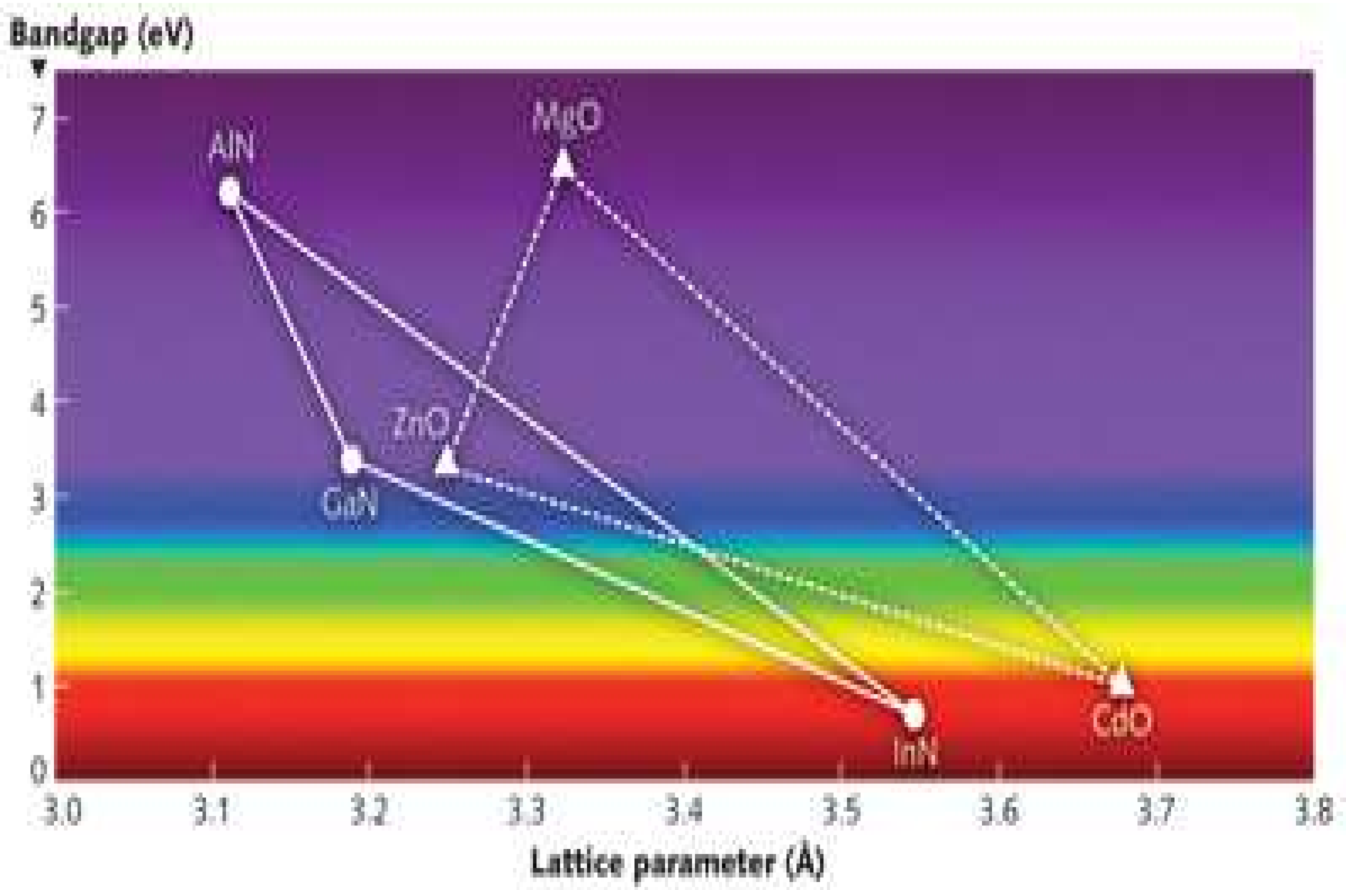


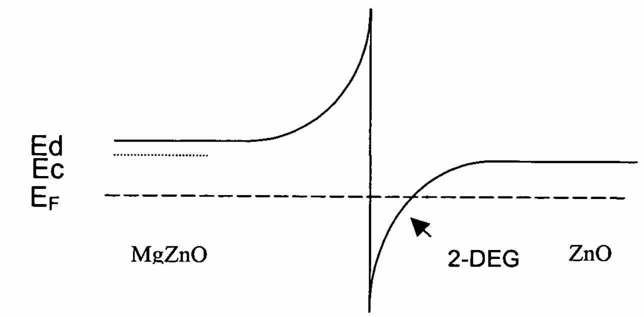
Figure of merit

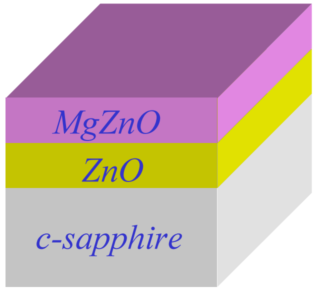
$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$

ZnO Bandgap Engineering & 2D Electron Gas

nanovation



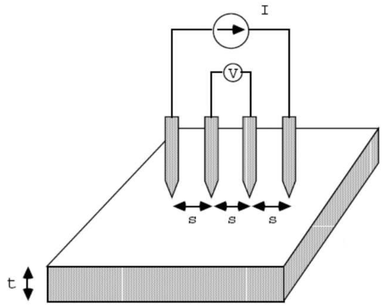




Rogers et al. Laser Focus World 49, 10 October (2013)

Impact of 2D Electron Gas at ZnO/MgZnO Interface

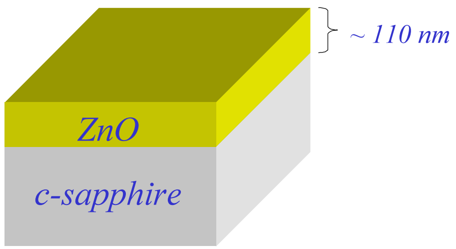
nanovation



$$\rho = \frac{\pi}{\ln 2}\ t\ \frac{V}{I} = 4{,}53\ t\ \frac{V}{I}$$

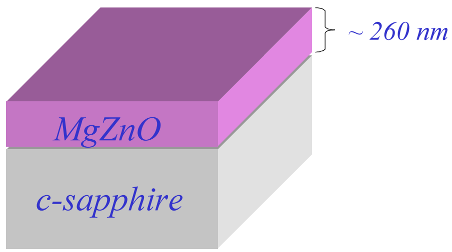
0.05 Ω.cm

ZnO/c-sapphire



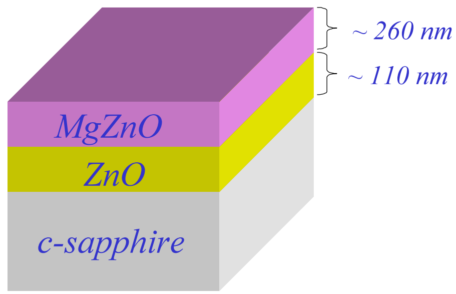
0.85 Ω.cm

MgZnO/c-sapphire



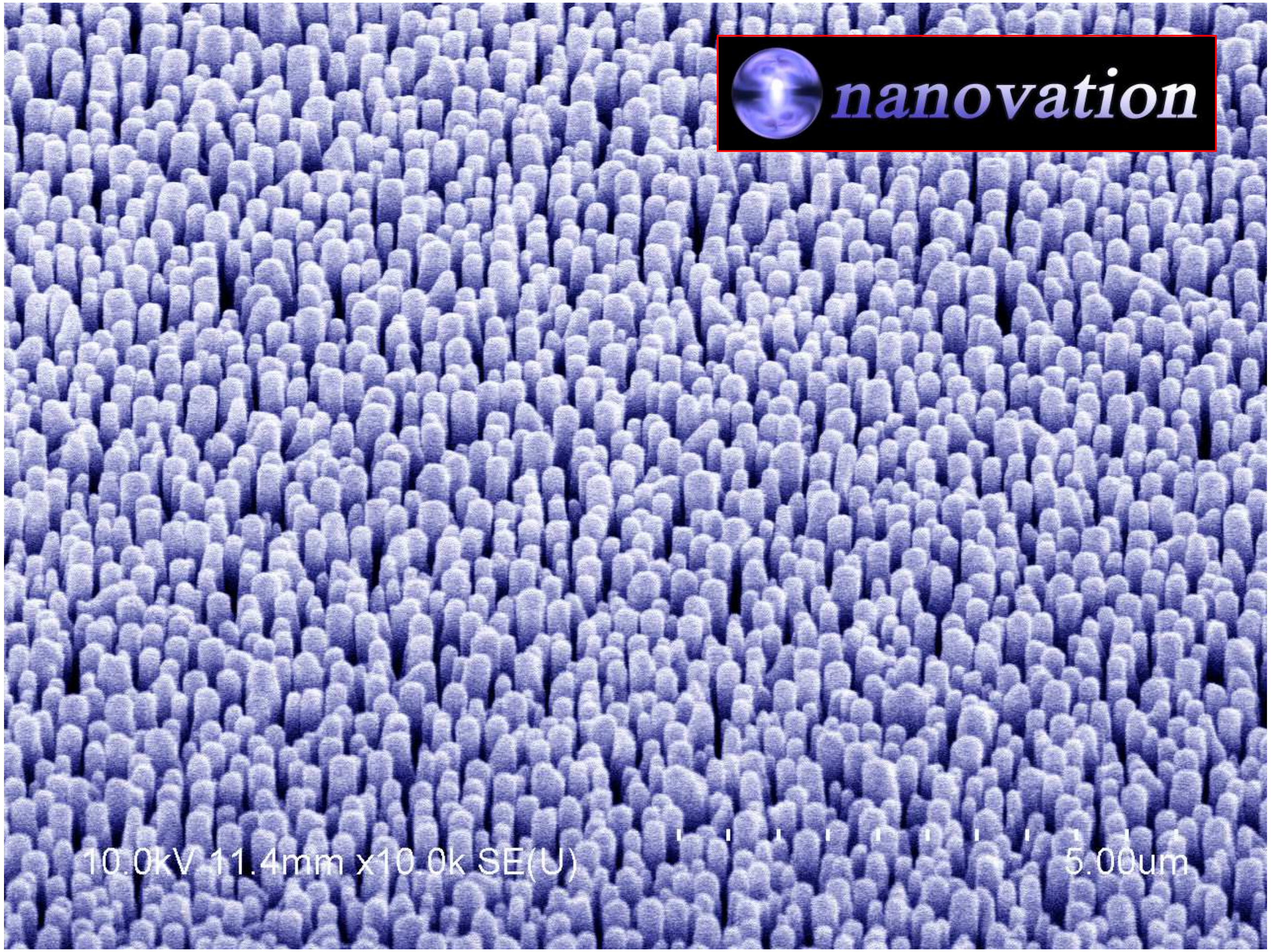
0.006 Ω.cm

MgZnO/ZnO/c-sapphire



Rogers et al. Proc. SPIE 8626 (2013) 86261X-1

Nano ZnO
Grown by PLD



p-type ZnO Thermoelectrics?

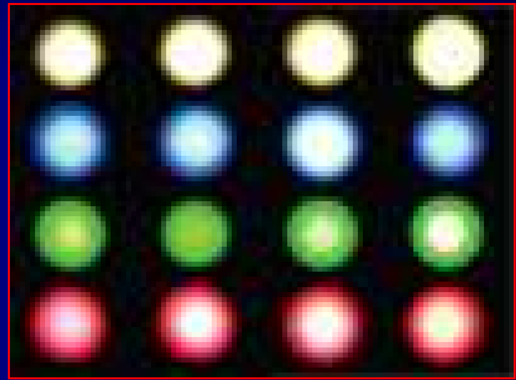
nanovation

Energy Challenges & Mechanics
- working on small scales

Aug. 2015

ZnO Homounction LEDs

EL λ_{max}	p-dopant	Reference
368 nm	As	Ryu et al.: Photonics West 2006
380 nm	P	Park et al.: II-VI conf. 2005
384 nm	N	Pan et al. : Photonics West 2006



Source: Ryu et al. Compound Semiconductor (2006)

Summary of p-type ZnO results

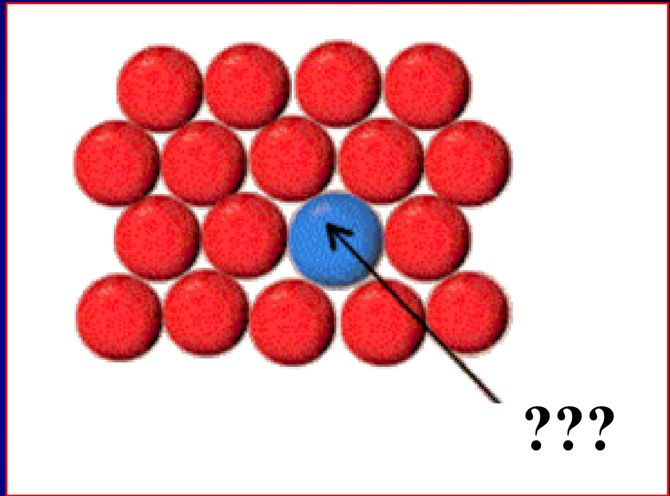
1) Many Dopants (N, As, P, Sb, Ag, Ga/N, Al/N, Li , Na, Zr/N)

2) Many Substrates (ZnO, sapphire (a, r ,c), glass, quartz, Si (111) & (100), GaAs, InP)

3) Many Growth Techniques

4) Relatively Low Mobility

5) Relatively High Resistivity



Fan et al. Prog. in Mater. Sci., (2013) & Choi et al. IEEE Trans Elec Devices, (2010)

Some problems with p-type ZnO development

1) Measurement issues

2) p-type response often unstable

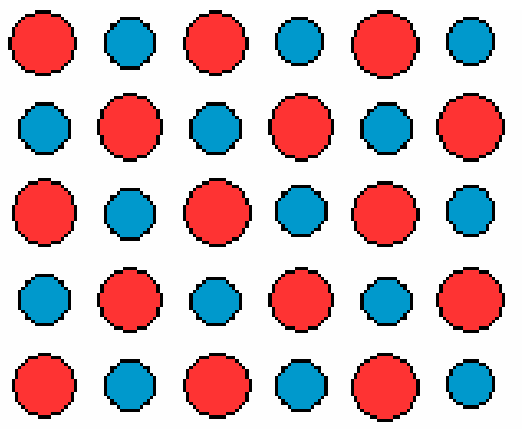
3) Strong intrinsic compensation
(oxygen vacancies, Zn interstitials, role of H)

4) Reproducibility issues

Native n-type Doping Compensation in ZnO

nanovation

Stoichiometric perfect crystal ➔ insulating

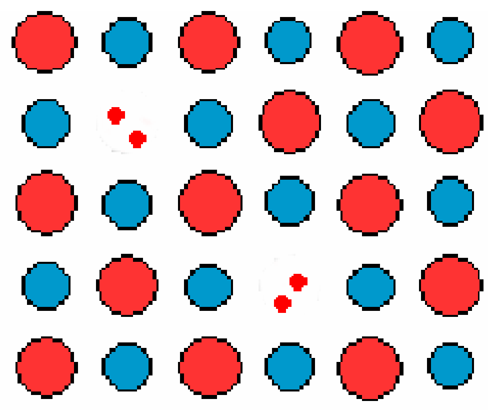


O^{2-}

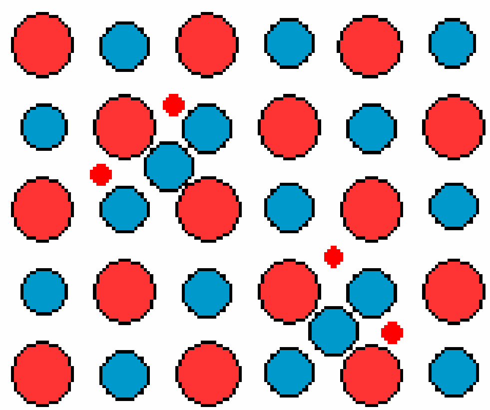
Metal Ion (e.g. Sn or Zn)

"Free" (or mobile) electron within the crystal.

ZnO generally oxygen deficient
➔ natively n-type doped…



Oxygen Vacancies



Interstitial Metal Ion

Interstitial hydrogen seems to be key in creating shallow donor in ZnO

C. Van der Waale

How about p-type MgZnO Thermoelectrics?

nanovation

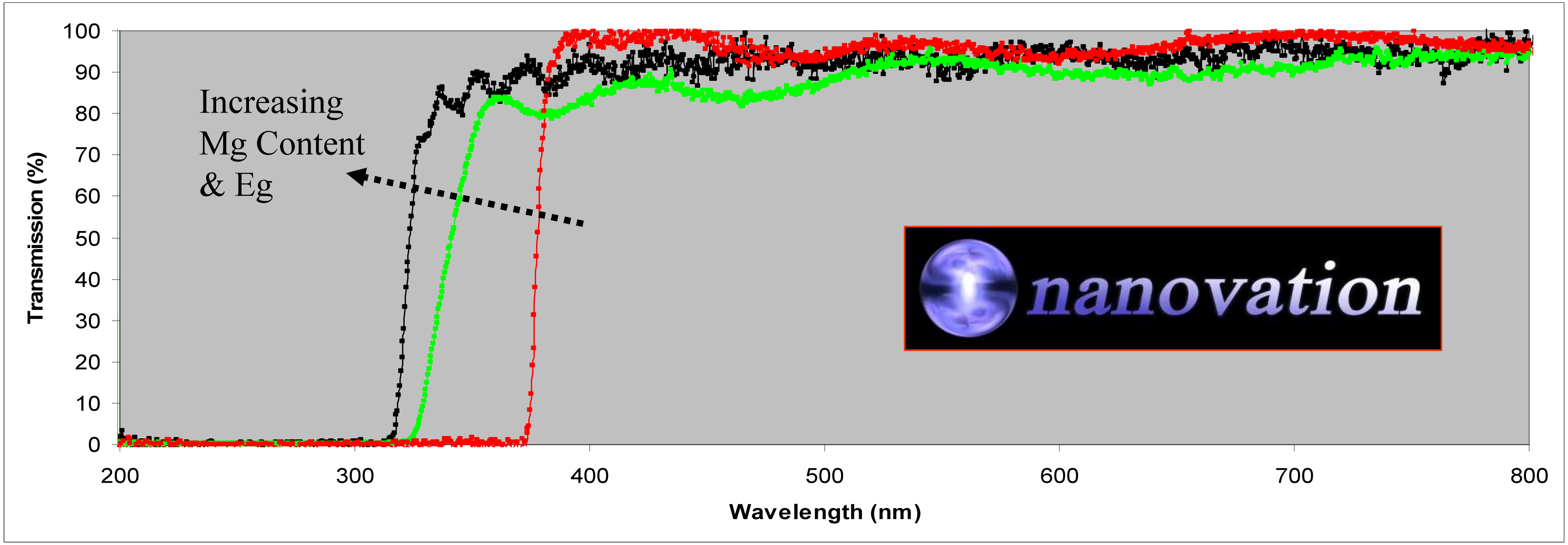
Energy Challenges & Mechanics
- working on small scales

Aug. 2015

MgZnO tuning of bandgap…

nanovation

Optical Transmission Spectra for MgZnO with various Mg Contents



1) Higher bandgap ➔ less n type compensation
2) V_{Zn} acceptor concentration increases with Mg content

} p-type doping a possibility

Rogers et al. Laser Focus World 49, 10 October (2013) *Rogers et al. Proc. SPIE 8626 (2013) 86261X-1*

5. Conclusions

Energy Harvesting Introduction

2001

Harvesting Method	Power Density
Solar Cells	15mW/cm^3
Thermoelectric	40µW/cm^3
Piezoelectric	330µW/cm^3

Atwood et al. *Proceedings of 14th Annual International Conference on Microelectromechanical Systems*, 2001, 357.

2012

Harvesting principle	Approximate power density
photovoltaic	10–100 mW cm^{-2}
thermoelectric	10–100 µW cm^{-2}
piezoelectric	1–10 mW cm^{-2}

Z. L. Wang, Angew. Chem. Int. Ed. 2012, 51, 2 – 24

Conclusions

ZnO Background

- highly multifunctional & a hot research topic
- electronics markets exist & are growing fast

ZnO Solar

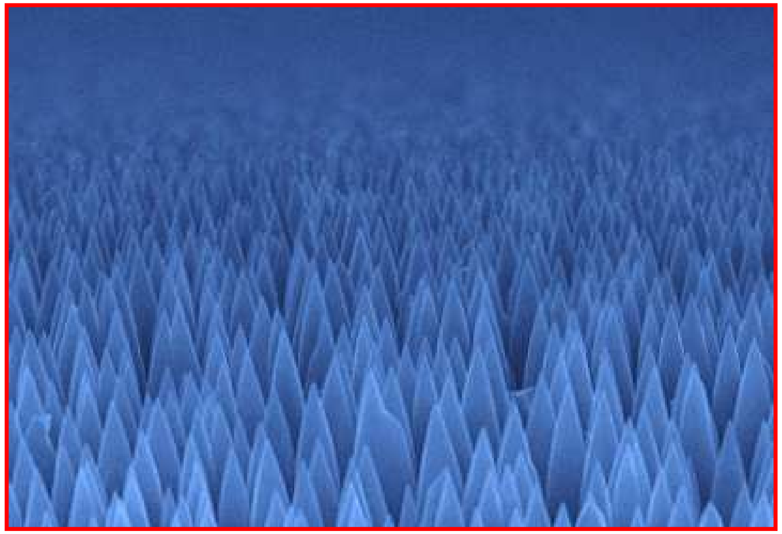
- ZnO present in many kinds of solar cells
- AZO replacing(toxicity & cost)

Nano ZnO Piezogenerators

- significant progress made
- market niche needed

ZnO Thermoelectrics

- early stage
- nano + 2DEG + p-type MgZnO potential



Rogers et al. Proc. SPIE 7605 (2010) 76050K-1

Acknowledgements

SUPA

RENATECH
french national network
of large technological facilities

ANR
AGENCE
NATIONALE
DE LA
RECHERCHE

CENTRE FRANCILIEN DE L'INNOVATION

La Centrale de
Technologie Universitaire

European Commission

SIXTH FRAMEWORK
PROGRAMME

SEVENTH FRAMEWORK
PROGRAMME

U.S.ARMY

Oxide-Based Materials & Devices Conference

SPIE Photonics West

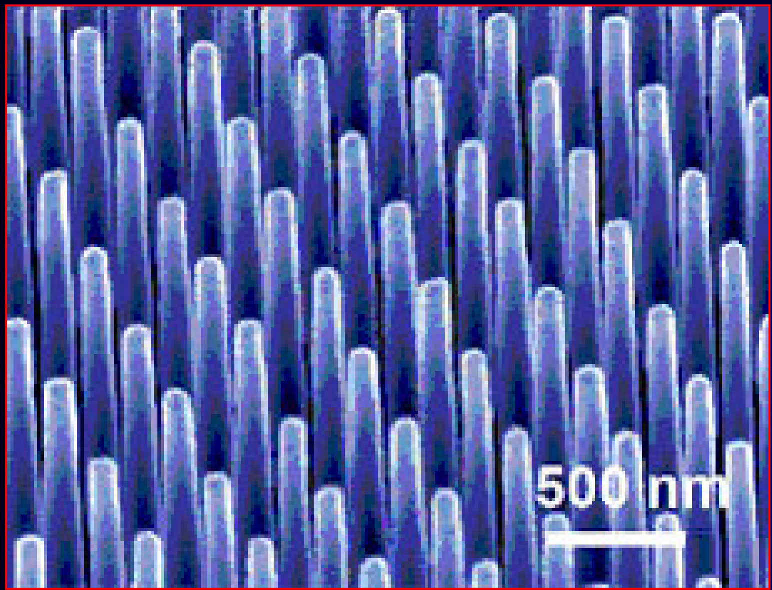
Feb. 2016, San Francisco

2015: 9th year

3 full days: 62 speeches + poster session, 28 countries

THANK-YOU!

nanovation



Erdelyi, Rogers, et al. Cryst. Growth & Design 11 (2011) 2515

nanovation

Questions?

www.nanovation.com

rogers@nanovation.com