P-type ZnO Thin Films: Present status

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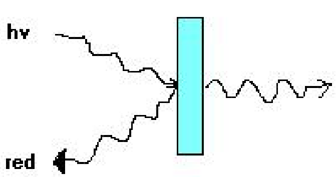


Semiconductor Laboratory, Dept.of Physics

18DEC2006

A brief introduction to TCO:

The first TCO: ITO : 1954

In_2O_3 Films by Rupprecht : $\sigma = 10$ S cm^{-1}, T= 60-65%

Present achievement is : $\sigma = 1.3 \times 10^{-4}$ S cm^{-1}, T= 89%

The search is for a High conducting, High transparency

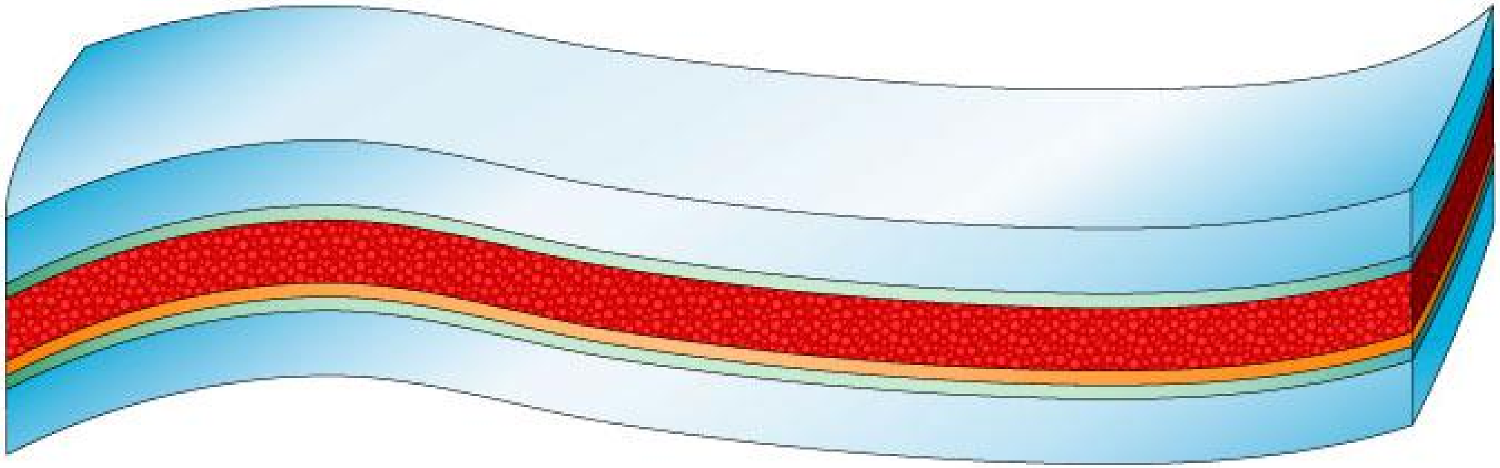
Limiting factor is the simultaneous conductivity
and transparency

Always it is a trade off between σ and T

There are more demands and more challenges
Hence there are more opportunities!

Organization:

- The TCO markets : gives us the chance to work
- Conventional TCO thin films : the basic physics and a review
- p- Type TCO thin films : A few challenges
- Zinc Oxide : The front line opportunity
- A few basic questions : keeps the researchers busy
- Concluding remarks



The International Conferences on TCO:

1. **International Symposium on Transparent Conducting Oxide, Heraklion, Crete, Greece.**
   ***Organisers*: FORTH-IESL**
   23-25 October 2006

   Email: kiriakid@iesl.forth.gr
   URL: www.iesl.forth.gr

2. The second International Symposium on Transparent Oxide Thin Films for Electronics and Optics (TOEO-2), November 8-9, 2001 at Tokyo
   Thin Solid Films Vol 411 (2002)

3. Every ICMCTF, AVS and SVC conferences have a special session devoted to TCO

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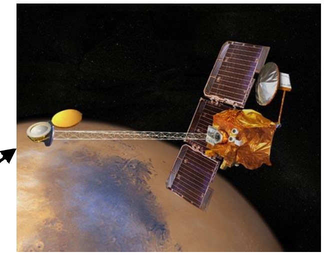
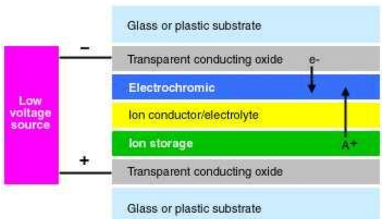
The TCO Markets:

In USA alone TCO Market is ~ 20 Billion

Flexible electronics ~12%

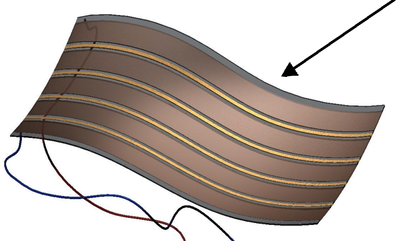
Space + Defence 12-15%





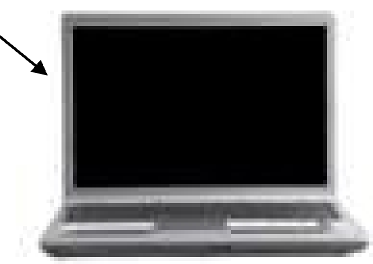
TCO

Electrochromics ~ 8%

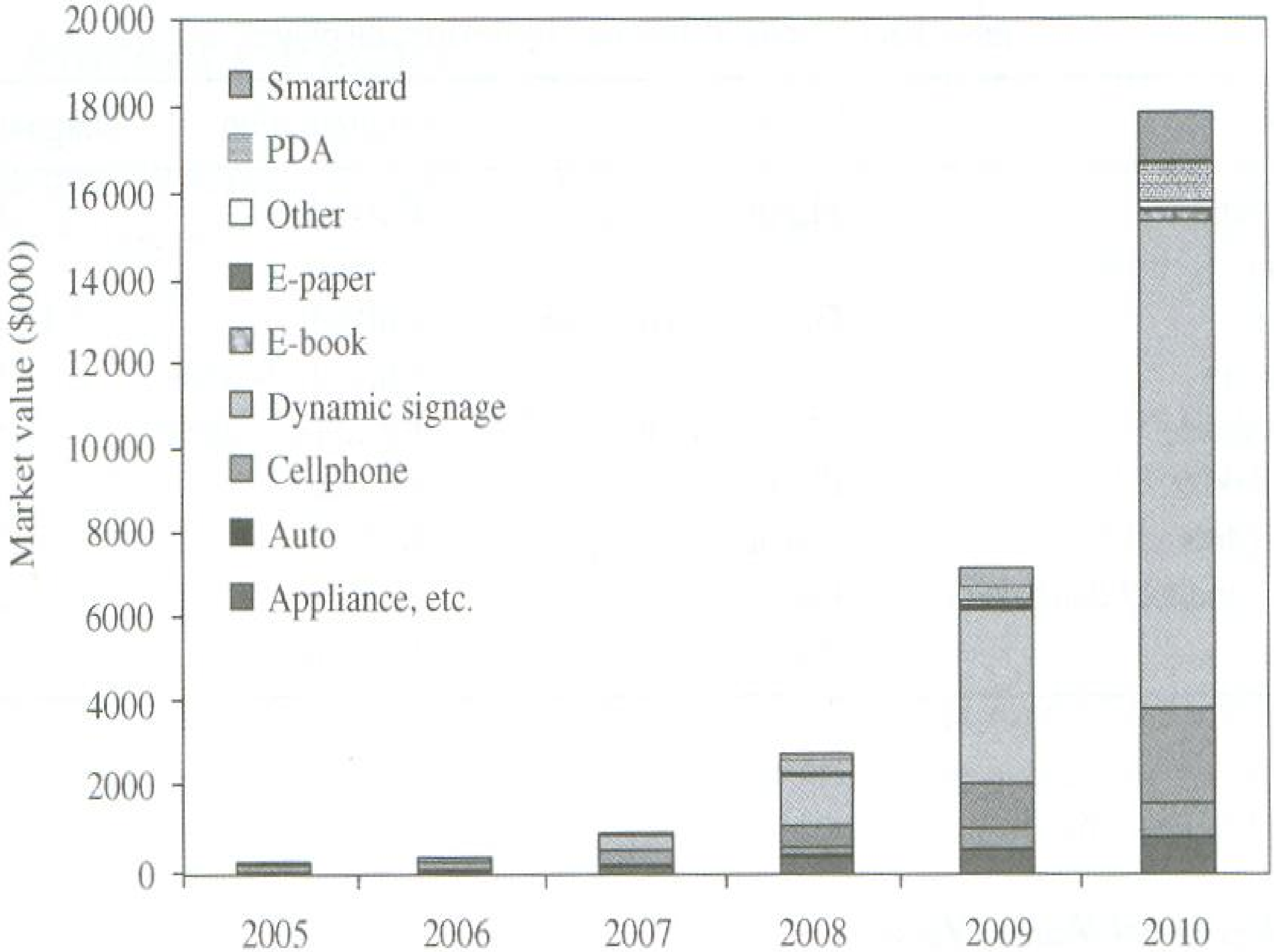


PV ~ 14%

LCD +PDP TV ~ 15%

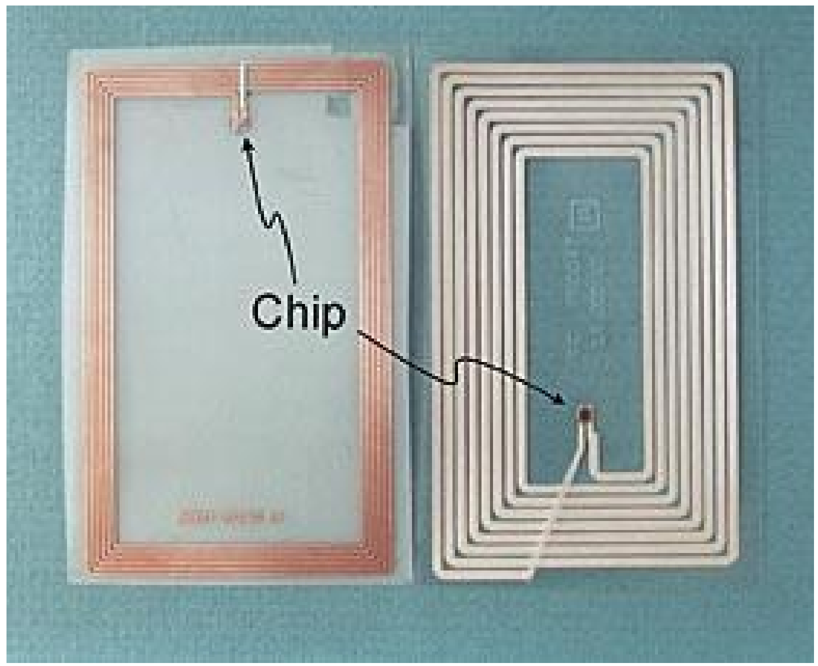


Lap Top 84%



Smartcard
PDA
Other
E-paper
E-book
Dynamic signage
Cellphone
Auto
Appliance, etc.
Market value ($000)
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
2005
2006
2007
2008
2009
2010

Flex circuits are planned for use in stacked-chip packages as well as single-chip packages (courtesy Tessera).



While polyimide is commonly used in most IC packages,
low-cost polyester is being used in the manufacture of high-volume,
single-chip "packages" like the RF ID tag shown

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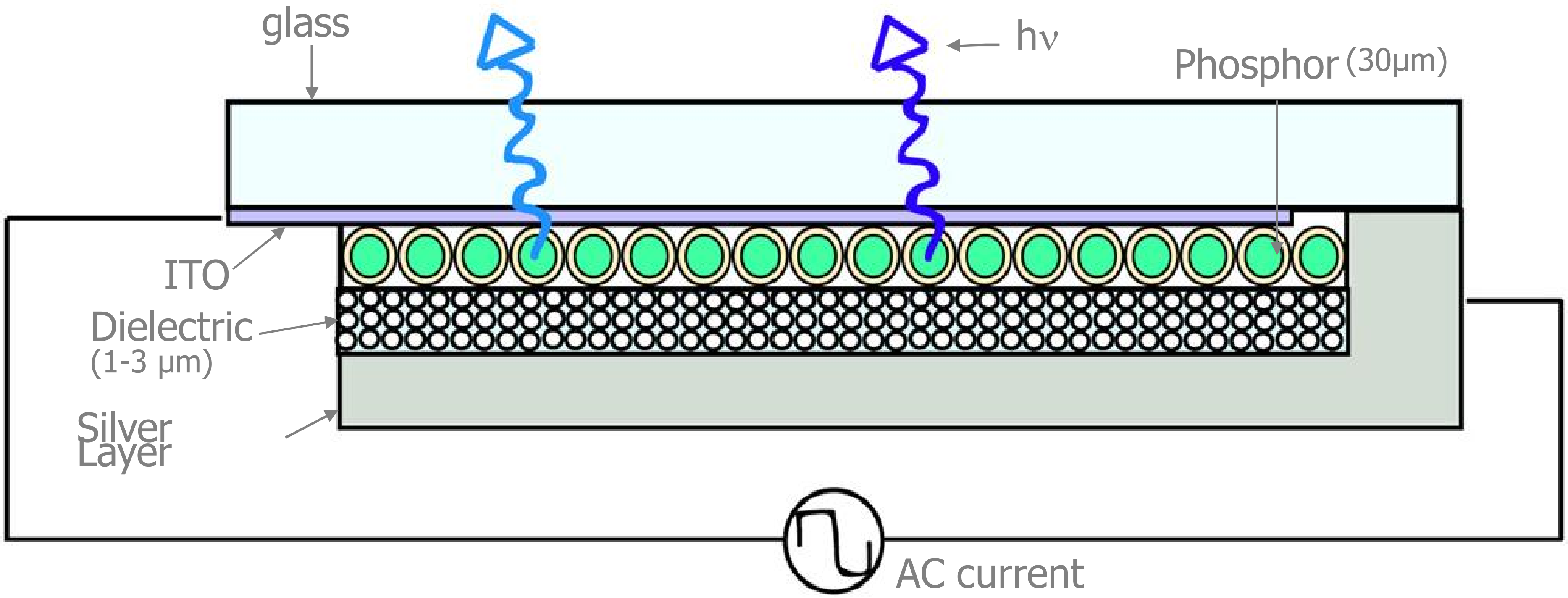
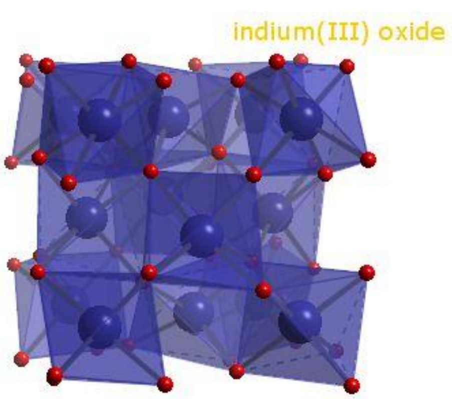
EL Lamps: Schematic

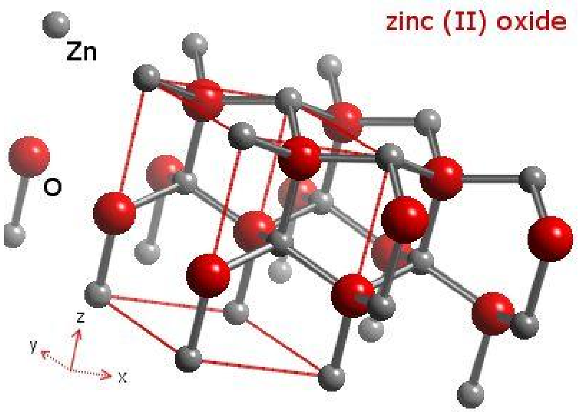


- The ITO and Silver layers act as two plates of a capacitor. The ITO is transparent, so the photons can pass through the layer.
- The AC current produces a changing electric field in the capacitor that excites the phosphor. The excited phosphors emit light.
- The dielectric evens out the E field, reflects light, and prevents the capacitor from shorting.

Basic Properties:

- N - type, Degenerate direct band gap semiconductors
- Eg = 3.0 - 4.1 eV
- Electron concentration ~ 10^{18} - 10^{21} /cc
- Infra red reflectors (metallic property)
- Radiation resistance to α,β,γ radiations
- Surface resistivity is very senstive to Oxygen or oxygen related species : alcohol
- Good adherence to many types of substrates : glass, plastic, polycarbonates, etc.





The conventional N-type:

Transparent Conductive Oxides

Material	σ (S cm^{-1})	n (cm^{-3})	μ_n (cm^2 V^{-1}s^{-1})
In_2O_3:Sn	10,000	> 10^{21}	35
ZnO	8,300	> 10^{21}	20
SnO_2	5,000	> 10^{20}	15

Reference: MRS Bulletin/August 2000

(*VERY* approximate, best-case poly, as assessed by J. F. Wager…)

Transparent Conductive Oxides

– Mobility assessment:

- μ_n (phonon-scattering) ~ 250 cm^2 V^{-1}s^{-1}
- μ_n (impurity-scattering) ~ 90 cm^2 V^{-1}s^{-1}

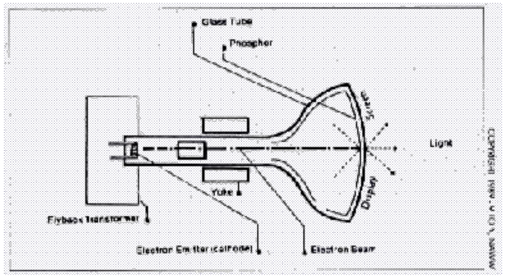
$$\therefore \mu_n \sim [250^{-1} + 90^{-1}]^{-1} \sim 66 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$$

Reference: R. G. Gordon, MRS Bulletin/August 2000

Applications of TCO thin films:

- **Passive Coatings:**
  - **Transparent electrodes (LCD, Flat Panel Displays and Plasma Displays)**
  - **Ohmic cotacts and optical couplers in Solar cells**
  - **Oxygen and alcoholic sensors**
  - **Infra red reflectors (Heat Mirrors) / Energy Efficient Windows**
  - **Electro-chromic windows**
  - **Nuclear reactor Windows**

Satellite Thermal barriers



EM Suppression

The search in N-type TCO is :

- Increase the carrier density ~ 10^{21}/cc
- Increase the Mobility ~ 30-40 $Cm^2/V\ s$
- Increase the Transmission ~ 85- 90 %
- Decrease the ionized impurity scattering

Most widely used Transparent Conductive Oxides

Material	Specific Resistivity µΩcm	Trans-mission	Costs	Process
In2O3:SnO2 (ITO)	110			DC/RF magnetron sputtering
ZnO:Al	260			Reactive MF magnetron sputtering
SnO2:F	490			

A few challenges:

ITO and FTO are not stable to Hydrogen and
Reducing Plasma

as encountered in Amorphous Solar cells and Plasma Displays

Indium diffusion is frustrating in Plasma Display manufacturing

Alternate is Zinc Oxide (AZO) : So heavy effort is on
Developing doped ZnO to compete with ITO

Doped ZnO wish to compete with conventional ITO
P-type is more easy in Spinel structures : ZnO has more advantages

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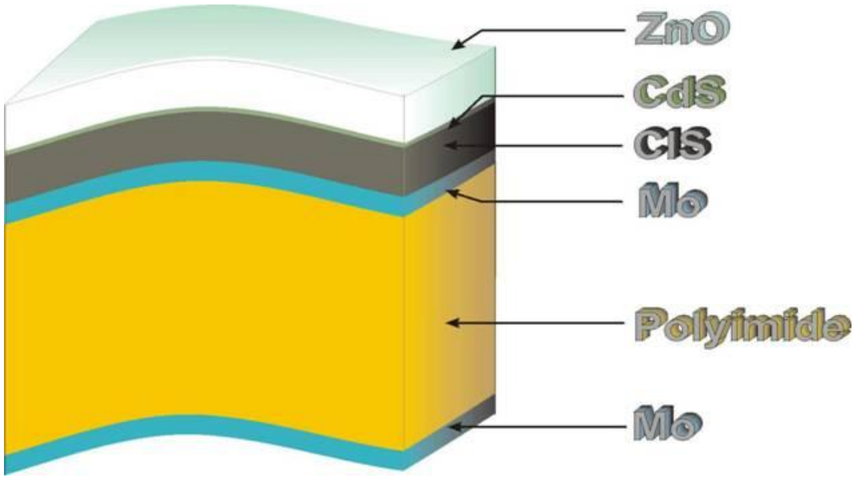

Zinc Oxide (ZnO) is a promising wide bangap semiconductor material

Other important properties of ZnO: piezoelectricity
biocompatibility
easy manufacturing of nanostructures

Potential technological applications of ZnO:
UV light emitting devices and sensors
transducers
biosensors

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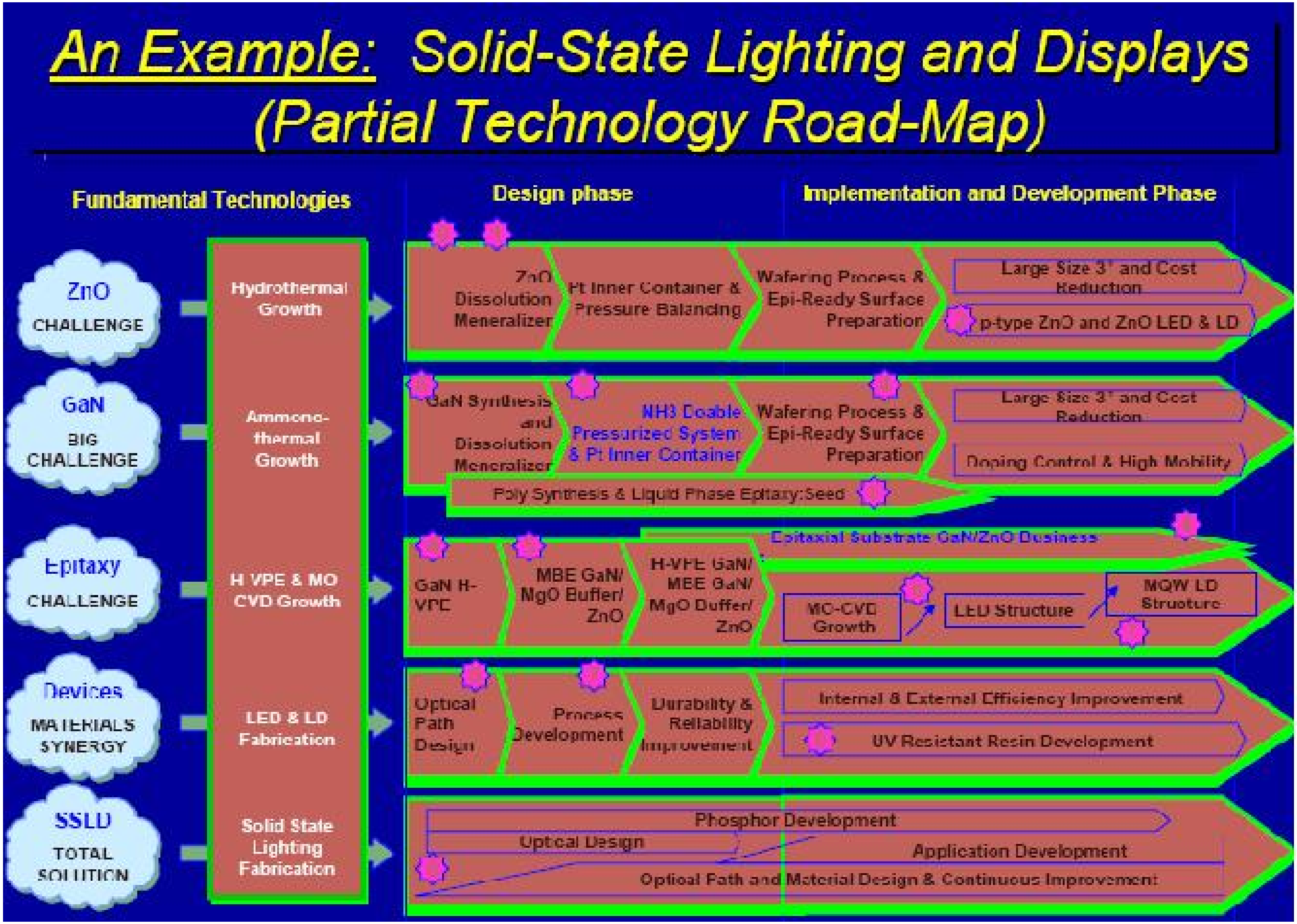

An Example: Solid-State Lighting and Displays
(Partial Technology Road-Map)
Fundamental Technologies
Design phase
Implementation and Development Phase
ZnO
CHALLENGE
GaN
BIG
CHALLENGE
Epitaxy
CHALLENGE
Devices
MATERIALS
SYNERGY
SSLD
TOTAL
SOLUTION
Hydrothermal Growth
Ammono-thermal Growth
H VPE & MO CVD Growth
LED & LD Fabrication
Solid State Lighting Fabrication
ZnO Dissolution Meneralizer
Pt Inner Container & Pressure Balancing
Wafering Process & Epi-Ready Surface Preparation
Large Size 3" and Cost Reduction
p-type ZnO and ZnO LED & LD
GaN Synthesis and Dissolution Meneralizer
NH3 Doable Pressurized System & Pt Inner Container
Wafering Process & Epi-Ready Surface Preparation
Large Size 3" and Cost Reduction
Doping Control & High Mobility
Poly Synthesis & Liquid Phase Epitaxy:Seed
Epitaxial Substrate GaN/ZnO Business
GaN H-VPE
MBE GaN/ MgO Buffer/ ZnO
H-VPE GaN/ MBE GaN/ MgO Buffer/ ZnO
MO-CVD Growth
LED Structure
MQW LD Structure
Optical Path Design
Process Development
Durability & Reliability Improvement
Internal & External Efficiency Improvement
UV Resistant Resin Development
Phosphor Development
Optical Design
Application Development
Optical Path and Material Design & Continuous Improvement

The p-Type TCO :

- Holes are the majority carries
- The TCO should have a suitable dopant
  - p-type concepts are very well understood from Silicon Physics
  - means, we must have more number of acceptor levels than donor levels
  - acceptor levels are a consequence of localization of covalent bond
  - Fermi level comes closer to valence band
  - Holes are heavier than electrons

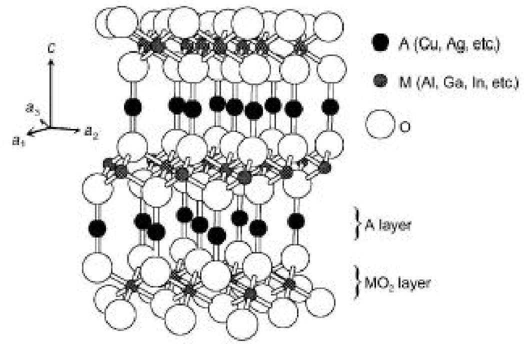
Requirements of p -type TCO

Chemical modulation of valence band : (CMVB)

- **The electronic configuration of the cationic species should preferably have a d10 s0 (d10 s2 systems did not yield positive results so far)**

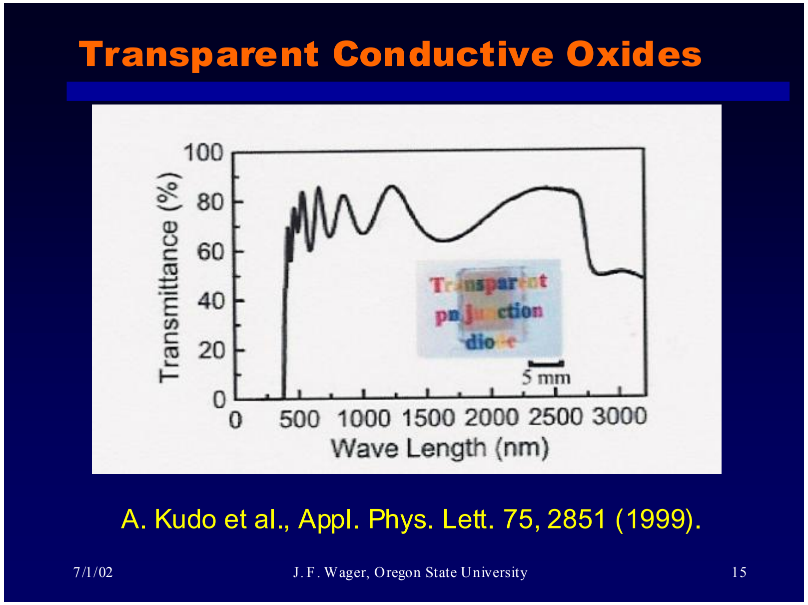
- **This condition is most suited for Cu+ and Ag+, the preferred crystal structure is Delafossite (of the type AMO2, where A is a monovalent cation and M is a trivalent positive ion)**

Localization of the covalent bond is the key issue



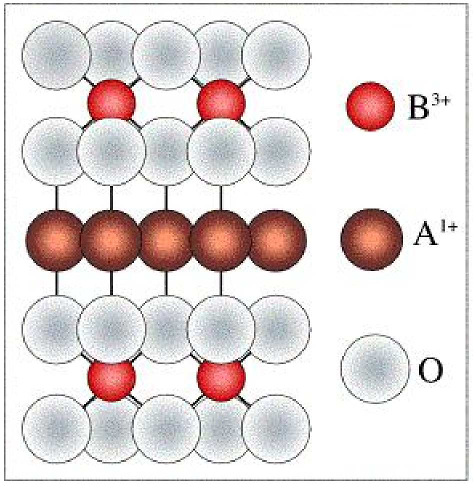
Localization of covalent bond

- Delafossite and Spinel structures involve both covalent and electro valent bonds
- The unit cells of these structures are quite complex
- The TCO material as such is having large number of defects
- How to achieve the localization of covalent bonds?



The materials being worked out are:

- Indium + Silver oxides
- Copper + Aluminium oxides
- Zinc oxide
- Oxy Sulfides and Sulphides



The Question is How to genarate Holes or Covalent states in the Crystal.

Localization of covalent bond

❖ Delafossite and Spinel structures involve both covalent and electro valent bond
❖ The unit cells of these structures are quite complex
❖ The TCO material as such is having large number of defects

How to achieve the localization of covalent bonds?

- A spinel structure (AB_2O_4) is suited for suitable modification to introduce a valence bond in the film
- What ever is being done with vacant s orbitals, similar tricks have to be done with the p orbitals of Oxygen

AB2O4

A = Divalent Cation (Metal : Zn, Cd)

B = Trivalent Cation (Metal : Al, Ga, In)

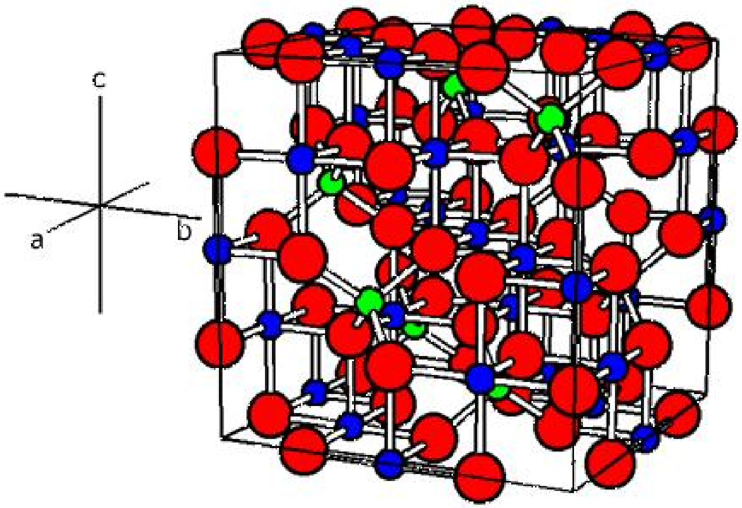
Spinel belongs to Cubic system

The unit cell contains

32 Cubic close packed Oxygen ior

08 Cations of A

16 Cations of B

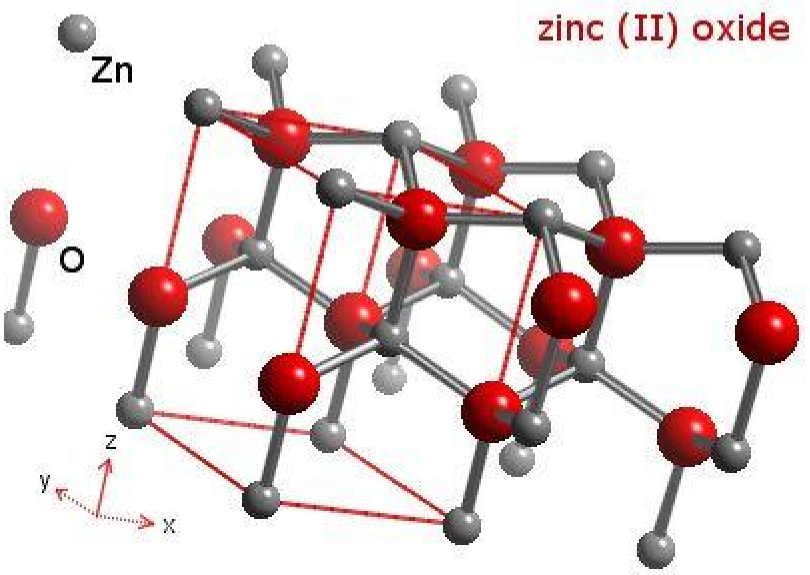


Compound	σ (S/cm)	μ (cm^2/Vs)	Laboratory
*$SrCu_2O_2$:K	0.048	0.46	Kudo *et al*. (1998)
$CuAlO_2$	0.3	0.13	Yanagi *et al*. (2000)
$CuGaO_2$	0.063	0.23	Ueda *et al*. (2001)
$CuInO_2$:Ca	0.0028		Yanagi *et al*. (2000)
$CuYO_2$:Ca	0.3 -1	<0.5	Jayaraj *et al*. (2000)
$CuScO_{2+y}$	30	<0.5	Duan *et al*. (2000)
$CuCrO_2$:Mg	220	<0.5	Nagarajan *et al*. (2000)

Material	Hole concentration	Mobility	Conductivity	Band Gap
	cm^{-3}	$Cm^2\ V^{-1}\ sec^{-1}$	$Ohm^{-1}\ cm^{-1}$	EV
ZnO:GaN_2	4×10^{19}	0.07	0.5	3
Cu_2SrO_2	$\sim 10^{18}$			
$CuAlO_2$	1.4×10^{18}	<1	1	3.5
$CuGaO_2$		<1		
$CuScO_2$		<1	1	
$CuYO_2$:Ca		<1	30	
CuI			40	3.1

Examples of Spinels:

- $ZnAl_2O_4$
- $ZnGa_2O_4$
- $ZnIn_2O_4$
- $CdAl_2O_4$
- $CdGa_2O_4$
- $CdIn_2O_4$

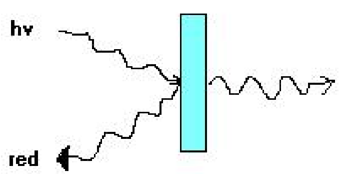


Localization of covalent bond

We have shown in Silver Oxide thin films that Oxygen plays an important role in Determining the type of conduction p- or n type (TSF 429 pp 129-134 (2003))

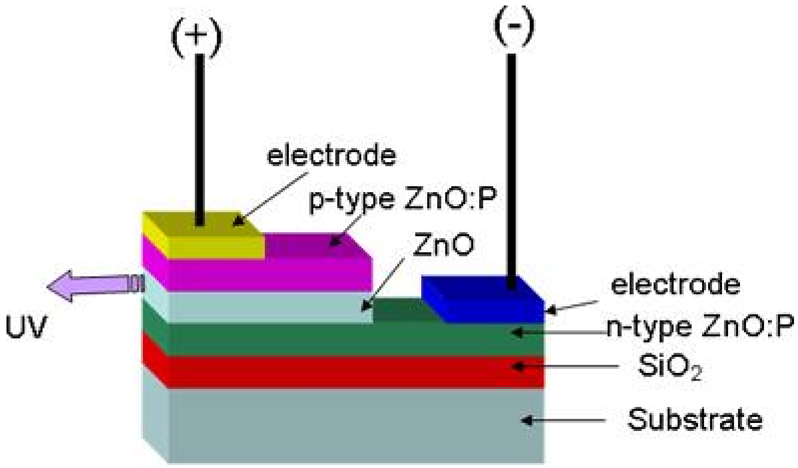
We tried to synthesize the p- type TCO from Silver Oxide + Indium Oxide
by reactive ebeam
and silver +Indium reactive DC Magnetron sputtering.

We have conducted an experiment with
Silver Oxide + Indium Oxide evaporated
by ebeam evaporation with a fixed oxygen flow in the chamber at three substrate temperatures.



Zinc Oxide :

- Zinc Oxide spinels have easy access to p- type
- Ga doping gives n - type ZnO
- Nitrogen doping gives p-type ZnO
- Codoping of Donor (Ga) and acceptor (N) seems to be more efficient
  - codoping compensates donors!



The main challenge in ZnO Thin Films is to synthesize

p- Type

P-type ZnO has been prepared by :

Doping with Nitrogen
Co-doping
Diffusion doping from substrate
Interface layer of the doping

Sb Doping of ZnO also gives p- type

Methods adopted :
Excimer Laser deposition
MOCVD
Filtered Vacuum Arc Deposition (FVAD)
DC magnetron Sputtering + Plasma Exposure

P type Zinc Based Oxides

	Year	Material	Method	Remarks	Author/ Group
1	1996	ZnO:N	ReactiveEvap-oration	Only N type	Sato, Akita Univ, Japan
2	1997	ZnO (excess Zn +NH3	CVD	P type	Minegishhi, Japan
3	1999	ZnO	Codoping	Theoritical	Yamatomo, Japan
4	1999	ZnO	Codoping Ga + N (N2O gas)	P – type	Joseph, Japan
5	2000	ZnO	PLD	Arsenic doping P type	Ryu, Missouri USA
6	2001	Cu and Zn based	RF Magnetron	p-n junction	Tate, Oregon, USA
7	2005	ZnO :N	MOCVD	P-type	Li,Asher,Coutts
8	2006	ZnO:N	DC Mag Sputtering	P-type	Subrahmanyam India

MOCVD

The best p-type ZnO film has low resistivity of 0.369 Ω-cm, high carrier density of 1.62×10^{19} cm^3, and mobility of 3.14 cm^2/V-s.

The obtained p-type ZnO films possess a transmittance of nearly 100% in the visible region and strong near-band-edge emission.

The p-type behavior of the samples should be due to the intrinsic acceptor like defects VZn, for ZnO film grown without nitrous oxide, and N, occupying O sites as acceptors for ZnO film grown with nitrous oxide

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NREL

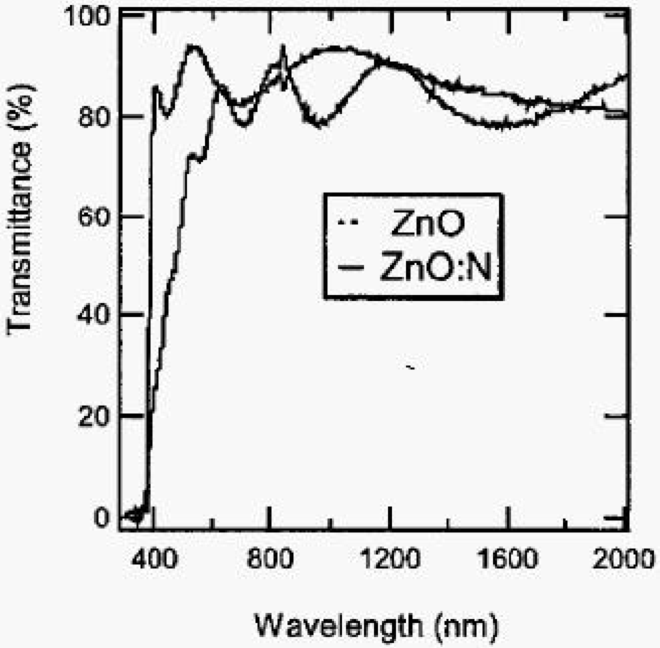


Figure 1. Optical transmittance spectra of ZnO and ZnO:N films deposited at 400°C.

Table 1. Electrical properties of ZnO films deposited at a temperature of 400°C.

Doping	C. C. (cm^{-3})	μ (cm^2/Vs)	ρ (Ω-cm)
ZnO	-8.42×10^{18}	3.2	0.235
ZnO	-8.38×10^{16}	6.3	11.8
ZnO:N	9.24×10^{13}	236	286
ZnO:N	8.36×10^{17}	4.55	1.64

MOCVD

Sb doping by FVAD:

Cathode Doping [at. %]	Sb at bulk [at. %]	O/Zn Ratio	Deposition time [s]	Thickness [nm]	ρ [$\Omega\cdot$m]	M [$m^2/(V\cdot s)$]	Carrier Density [m^{-3}]	Type
0	0	0.68±0.03	60	430	$0.11\cdot10^{-3}$	$11.6\cdot10^{-4}$	$3.77\cdot10^{25}$	n
3	1.5±0.3	0.721±0.03	120	330	$156\cdot10^{-3}$	$8.56\cdot10^{-4}$	$4.65\cdot10^{22}$	p
3	1.45±0.3	0.724±0.03	240	500	$283\cdot10^{-3}$	$21.45\cdot10^{-4}$	$1.03\cdot10^{22}$	p

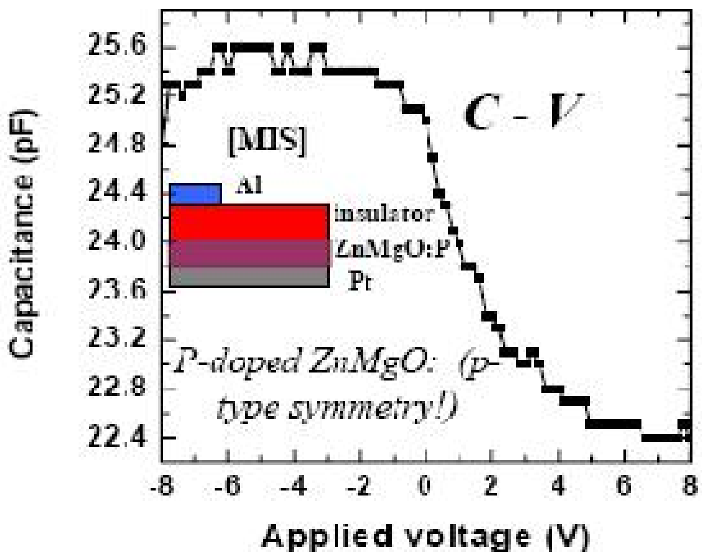


Fig. 1. Capacitance-voltage characteristics of P-doped (Zn,Mg)O MIS diode showing p-type behavior.

The summary:

Nitrogen in ZnO can give p- type
Compensation mechanism
So, the conduction will be Bipolar

Then, How to measure the carrier Density and Mobility?

A fundamental question

The next View graphs explain the methods to measure the Hole concentration.

Major difference in concept with Silicon Physics:

- Si is pure: material is perfectly ordered
- The dopant in Si introduces required carriers : n or p
- The majority carriers are always 5 - 6 orders of magnitude more than minority carriers
- TCO is highly disordered material

Hall Effect:

- When both electrons and holes contribute for conduction, measurement of Hall Voltage is very difficult

$$R_H = \frac{(p\,\mu^2{}_p - n\,\mu^2{}_n)}{q\,(p\,\mu_p - n\,\mu_n)^2}$$

Bipolar conduction

- Quantitative Mobility Spectrum Analysis (QMSA) developed by Naval Research laboratory
- Depends upon (Magnetic) Field dependent Hall Measurements
- Applied for GaAs and InP : Mobilities are very very high (~ 10^3 to 10^4 cm^2/Vs)

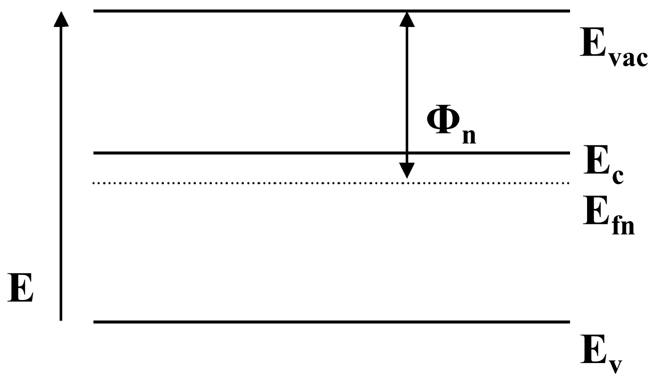
We propose to measure the P-type conductivity by Kelvin Probe

Contact Potential Difference (CPD)

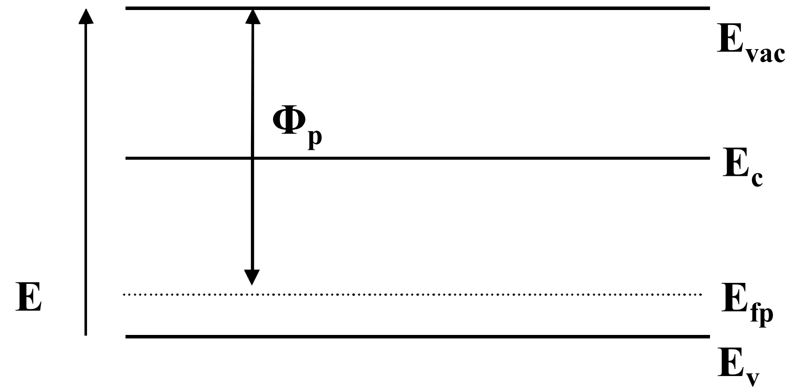
We worked on thee measurement of CPD of magnetron sputtered ZnO and treating the surface with Nitrogen Plasma

Results are Positive.

Energy Band Diagrams



N-Type Semiconductor

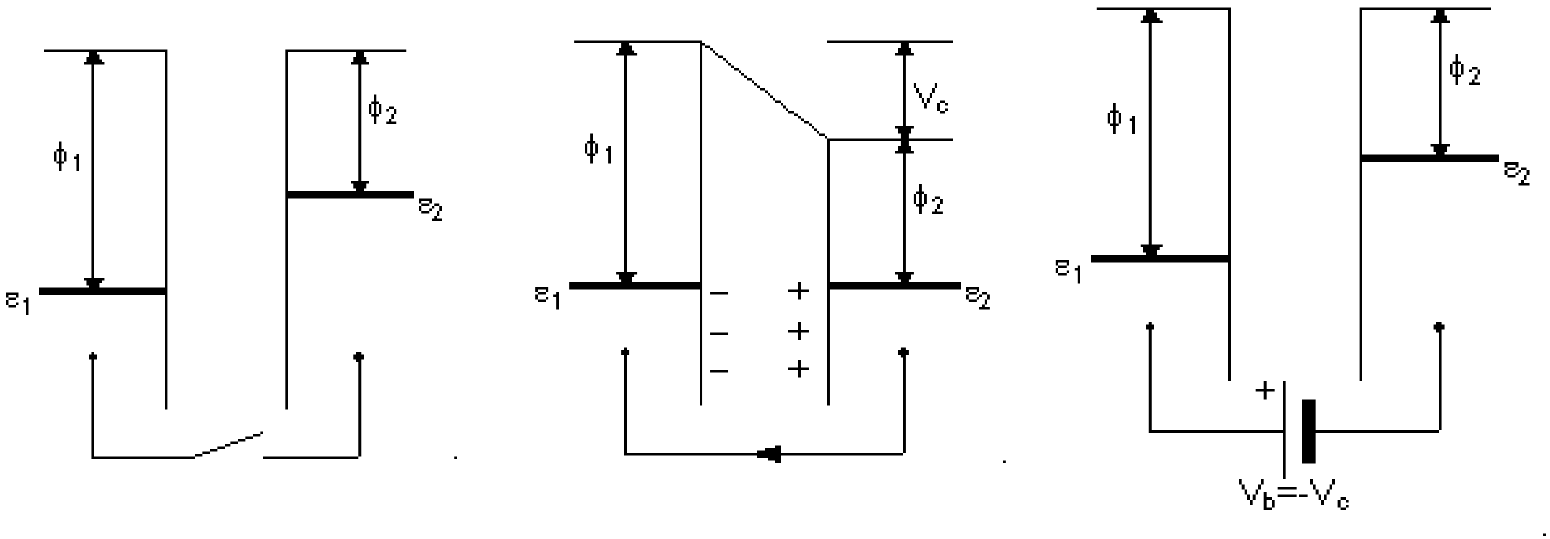


P-Type Semiconductor

The measurement of Surface work function of TCOs :

Basic principle:

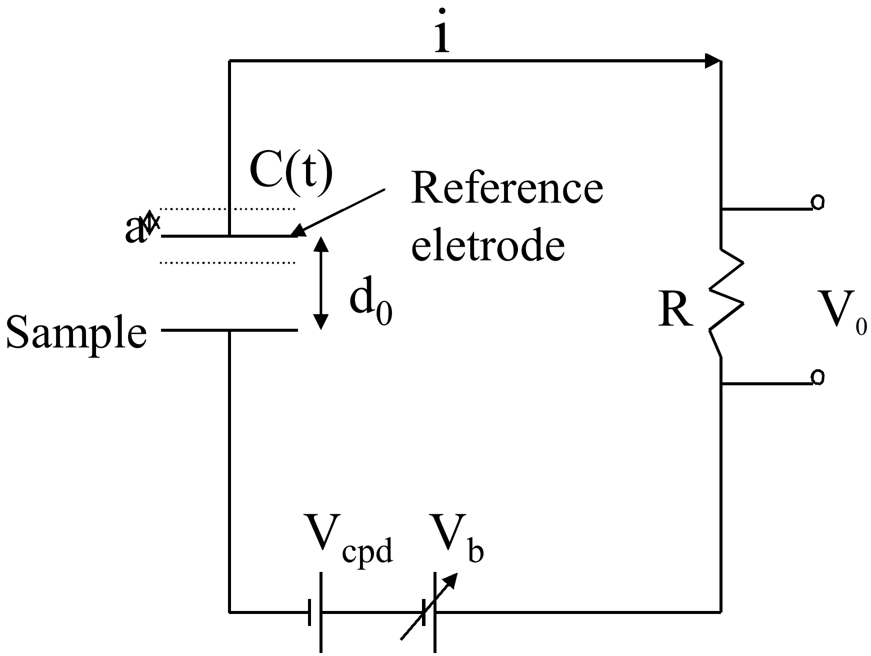
- Eenergy level diagrams for two conducting specimens

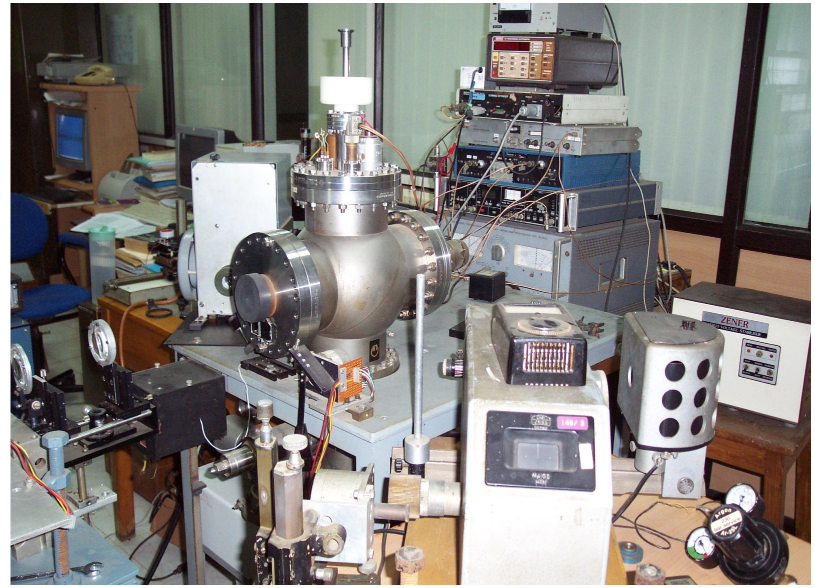


(a) (b) (c)

$$qV_C = \Phi_1 - \Phi_2$$

The basic measuring circuit arrangement





$$i = \frac{dq}{dt} = \frac{d(CV)}{dt} = V\varepsilon_0 A \frac{d}{dt}\left[\frac{1}{d_0 + aSin(\omega t + \phi)}\right]$$

$$C = \frac{\varepsilon_0 A}{d} = \frac{\varepsilon_0 A}{d_0 + aSin(\omega t + \phi)}$$

Nernst coefficient:

- In Nernst Coefficient measurement, Nernst field (E_y) is developed (similar to Hall Voltage) due to Magnetic Filed and Temperature gradient

- $E_y = - Q (\partial T / \partial x) B_z$

Present status:

- Report of Hole concentration and Mobility are not really accurate (by Hall Effect)
- Transparency is rather low (30 -40% at 550 nm)
- The transport mechanism is not clear yet
- Most important: NO TESTED RECEPIE IS AVIALABLE FOR MAKING P-TYPE !!

For accurate measurements:

- The type determination is to be confirmed by Seebeck Coefficient
- The carrier concentration is to be derived from systematic measurements of Nernst Coefficient measurements
- Scattering effects have to be evaluated carefully
- If hole concentration is considerably high (> 10^{20} to 10^{21}/ cc), nonlinear effects may take place!

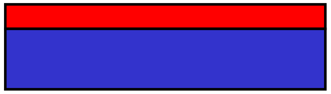
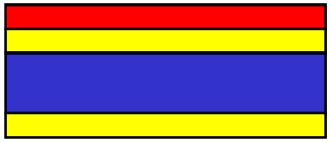
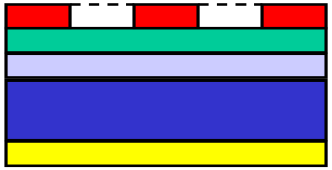
The flexible electronics require

- Good TCO (High σ, high t) to be coated at low temperature on Plastic substrates

- Active devices require the work function measurement on p and n type TCOs

Accentia™
Standard Product ITO Resistance Capability

Ohms per square

Product	Structure	Layers	40	60	100	200	250	300	310	350
G430300		ITO PET	S	S	S	S	S	S	S	
G901300		ITO Hard Coat PET Hard Coat			S				S	S
G901400		ITO Gas Barrier Under Coat PET Over Coat	S	S			S	S		

Custom Resistance →

S = standard product
> 350 ohm/sq.: specification has to be defined

Sheldal

Organization:

- The TCO markets : gives us the chance to work
- Conventional TCO thin films : the basic physics and a review
- p- Type TCO thin films : A few challenges
- Zinc Oxide : The front line opportunity
- Flexible Electronics : Emerging and more powerful field
- A few basic questions : keeps the researchers busy
- Concluding remarks

- Do we have a recipe for
  Tailor made conductivity, transmission refractive index and band gap ?

- Can we have a confirmed recipe for p-type ZnO?

- Why PVD techniques do not yield good p- type ZnO?

- What is the Physics of the TCO which makes it radiation hard?

- Can we achieve graded refractive index for TCO for Stealth technology?

- How to stop diffusion of In in high temperature processing (for PDPs)?

Thanks for your time, attention and Concern.

A special thanks to the Organizers of IJW 2006
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