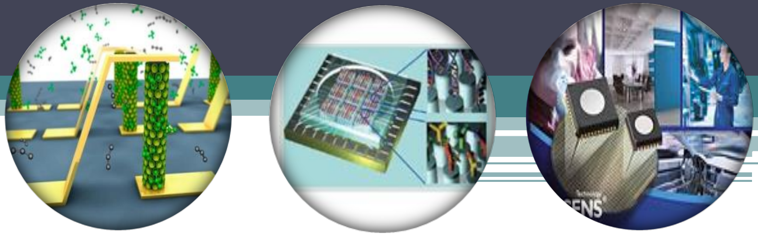
고려대학교 2018.11.28

Spectroscopic Interpretation of Transparent Oxide Films for Various Applications



Kwun-Bum Chung

Division of Physics and Semiconductor Science, Dongguk University

E-mail : **kbchung@dongguk.edu**

Advanced Physics on
Electromaterial Laboratory

dongguk
UNIVERSITY

Introduction of CV

Career

BS, Physics, Korea University (1996~2000)
MS/PhD, Physics, Yonsei University (2000~2006)
Post-Doc., KRISS (2006~2007)
Post-Doc., NC state University (2007~2009)
Assistant Prof., Physics, Dankook University (2009~2014)
Associate Prof., Physics, Dongguk University (2014~

Research Interests

Insulating oxides

- “Suppression of defect states in HfSiON gate dielectric film on n-type Ge(100) substrates” , Applied Physics Letters 93, 182903 (2008)
- “Effects of surface chemical structure on the mechanical properties of Si1-xGex nanowires” , Nano Letter 12, 1118 (2013) 외 50 여편

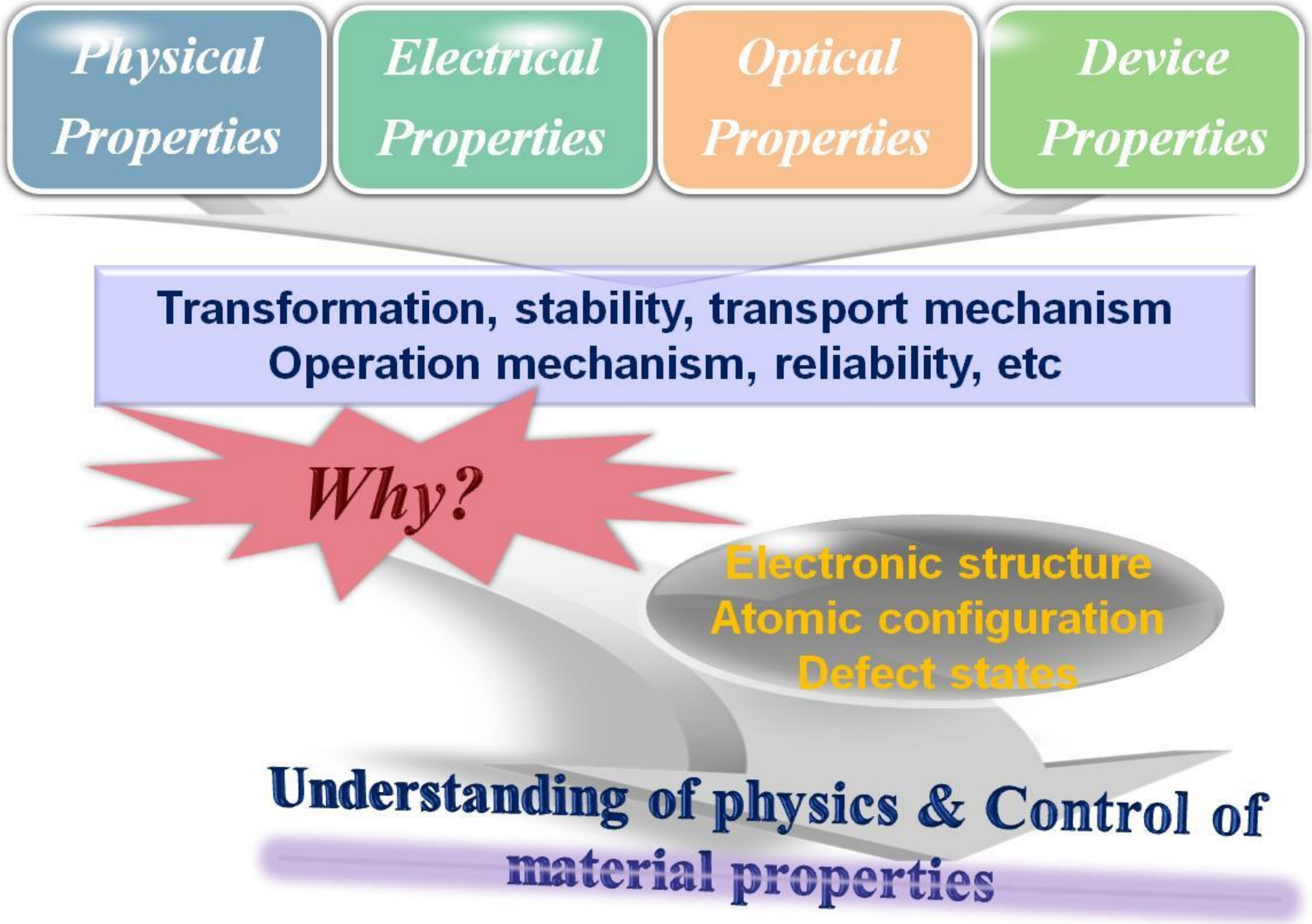
TCO & TOS

- “Enhancement of device performance and stability with homojunction structured tungsten doped InZnO thin film transistor” , Scientific Reports 7, 11634 (2017)
- “Unraveling the Issue of Ag Migration in Printable Source/Drain Electrodes Compatible to Versatile Solution-Processed Oxide Semiconductors for Printed Thin-Film Transistor Applications” , ACS Applied Materials & Interfaces 9, 14058 (2017)
- “Activation of sputter-processed indium-gallium-zinc oxide films by simultaneous ultraviolet and thermal treatments” , Scientific Reports 6, 21869 (2016) 외 80 여편

Application & Analysis

- “A transparent solar cell based on a mechanically exfoliated GaTe and InGaZnO p–n heterojunction” , Journal of Materials Chemistry C 5, 4327 (2017)
- “Layer-by-Layer Assembled Graphene Multilayers on Multidimensional Surfaces for Highly Durable, Scalable, and Wearable Triboelectric Nanogenerators” , Journal of Materials Chemistry A 6, 3108 (2018)
- “Electron blocking layer-based interfacial design for highly-enhanced triboelectric nanogenerators” , Nano Energy 50, 9 (2018)
- “Area-selective Atomic Layer Deposition using Si Precursors as Inhibitors” , Chemistry of Materials 30, 7603 (2018) 외 40 여편

Research topics



Physical Properties

Electrical Properties

Optical Properties

Device Properties

Transformation, stability, transport mechanism
Operation mechanism, reliability, etc

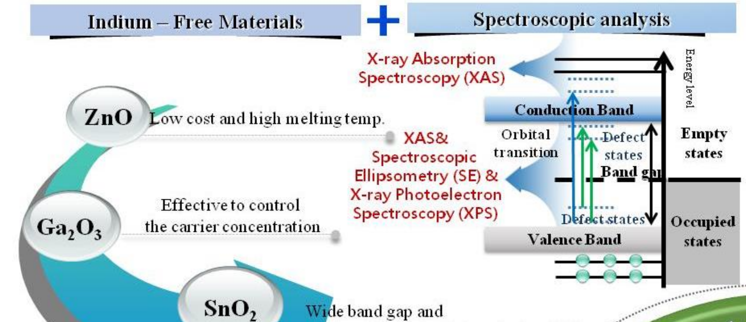
Why?

Electronic structure
Atomic configuration
Defect states

Understanding of physics & Control of material properties

Research topics

Electronic Structure of Transparent Oxide Films



Indium – Free Materials + Spectroscopic analysis

ZnO Low cost and high melting temp.

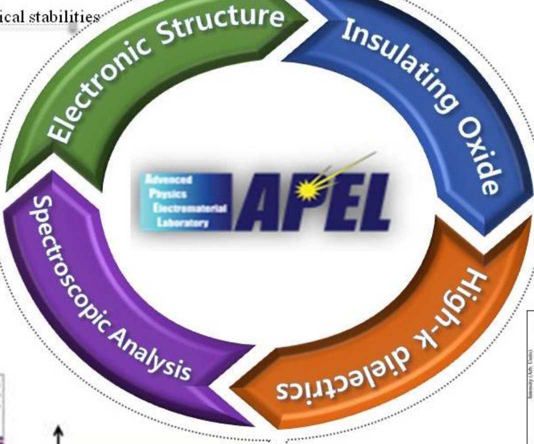
Ga_2O_3 Effective to control the carrier concentration

SnO_2 Wide band gap and the best thermal and chemical stabilities

X-ray Absorption Spectroscopy (XAS)

XAS& Spectroscopic Ellipsometry (SE) & X-ray Photoelectron Spectroscopy (XPS)

Semiconductor properties of GZTO can be explained using spectroscopic analysis for each binary oxide in GZTO films



Insulating Oxide for high mobility device and power device

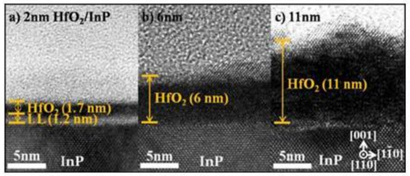


FIG. 1. Color online HR-TEM images of HfO2 films grown on BOE treated InP with film thicknesses of a 2 nm b 6 nm, and c 11 nm, respectively.

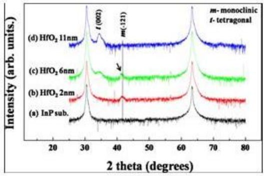


FIG. 2. Color online XRD data for HfO2 films as a function of film thickness.

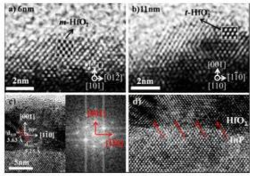


FIG. 3. The monoclinic structure is transformed into atetragonal structure. when the film thickness increases from 6 to 11 nm. The simulated image is in good agreement with the crystalline HRTEM images.

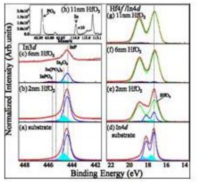
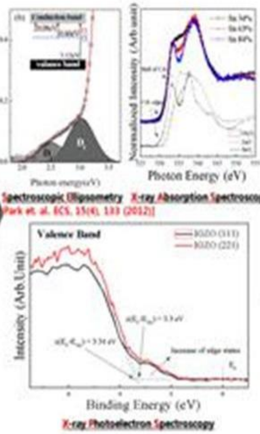


FIG. 4. Color online HR-XPS core-level spectra of In 3*d left side and* Hf 4*f / In 4d right side in HfO2 / InP*.

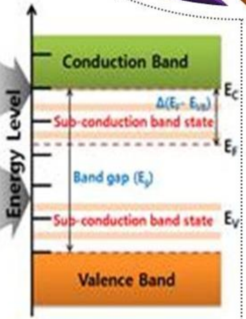
Spectroscopic Analysis of Multi-Functional Materials



Spectroscopic Ellipsometry X-ray Absorption Spectroscopy

[H.W. Park et. al. ECS, 15(4), 133 (2012)]

X-ray Photoelectron Spectroscopy



High-k dielectrics

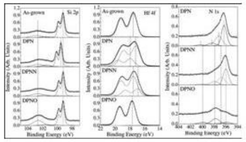


FIG. 1. XPS spectra a Si 2*p, b Hf 4f, and c N 1s, as a function of various* annealing conditions.

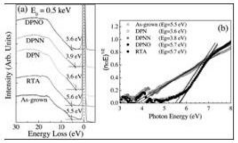


FIG. 2. A *Eo=0.5 keV. Band gap using b spectroscopic ellipsometry* is well consistent with the REELS data.

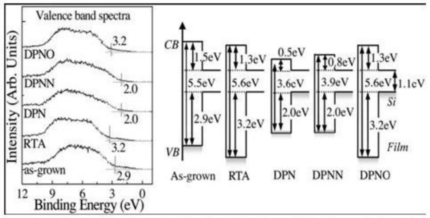


FIG. 3. Valence band spectra for the HfO2 films left side and a band alignment diagram with Si right side as a function of various postannealing treatment.

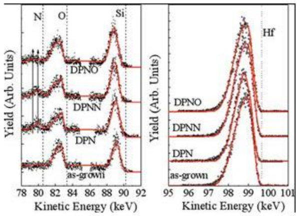


FIG. 4. Color online MEIS spectra for a change in concentration in the depth direction as a function of postannealing treatment.

Contents

Introduction

Electronic structure

Experimental results

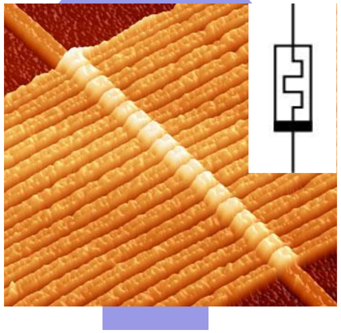
- Transparent Conducting Oxides (TCO)
- Transparent Oxide Semiconductors (TOS)
- Transparent Oxide Thin Film Transistor (TTFT)

Applications

Diverse Applications of Oxide Films

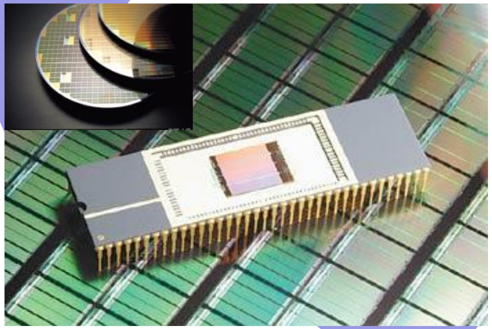
Oxides Films

Memristor



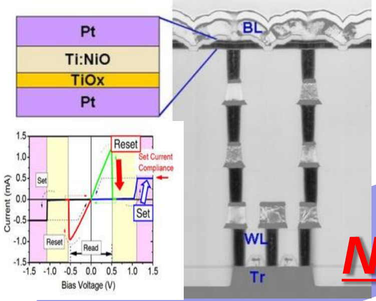
Coating

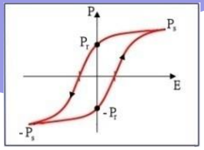
CMOS, Memory



TCO, OTFT

Non-volatile memory

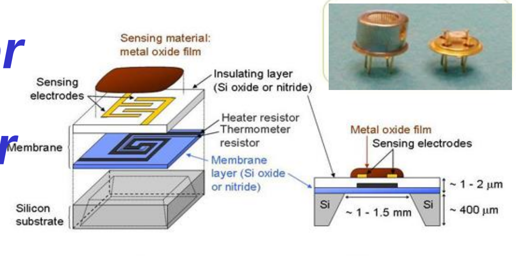




Solar energy application

Gas sensor

Bio sensor



Top view

Side view

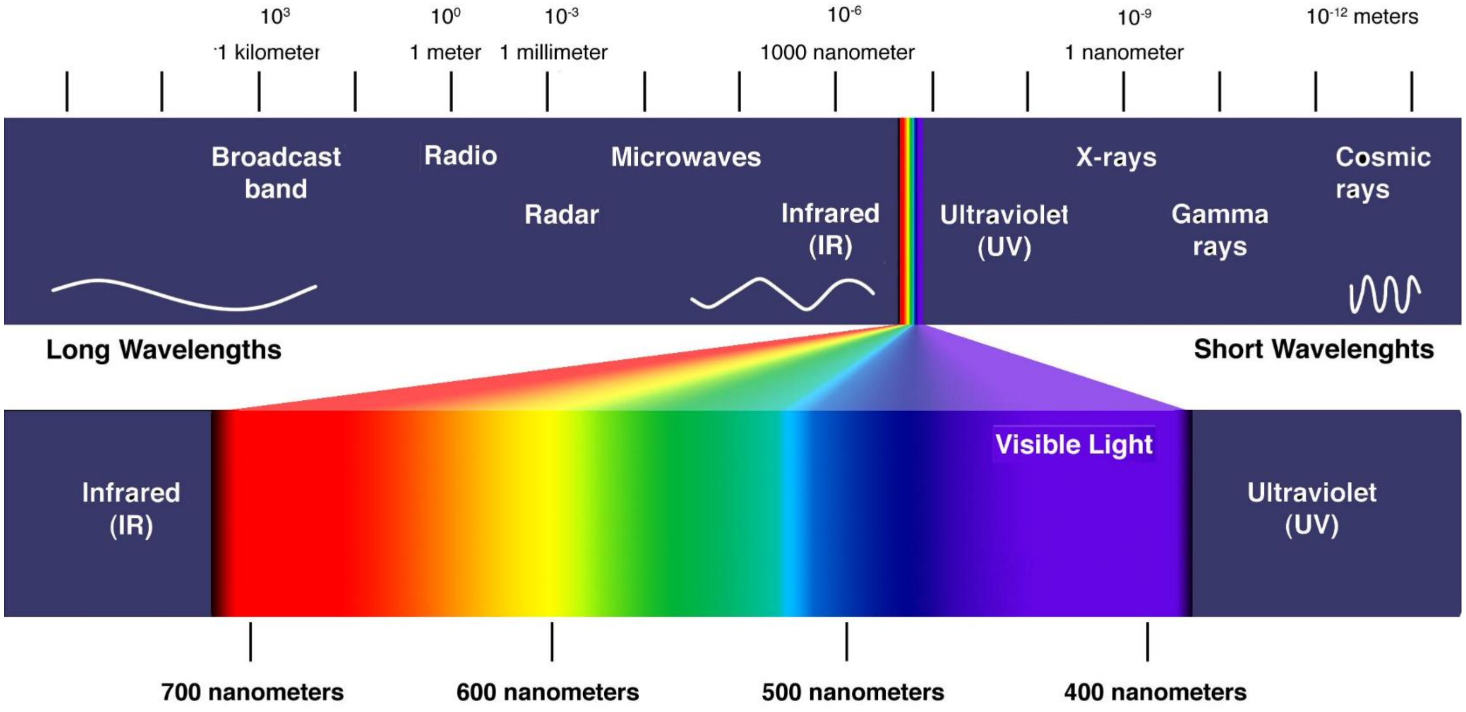
Diverse Applications of Transparent Oxide Films

Transparent OLEDs

Transparent LCDs

OPVs

Transparency?



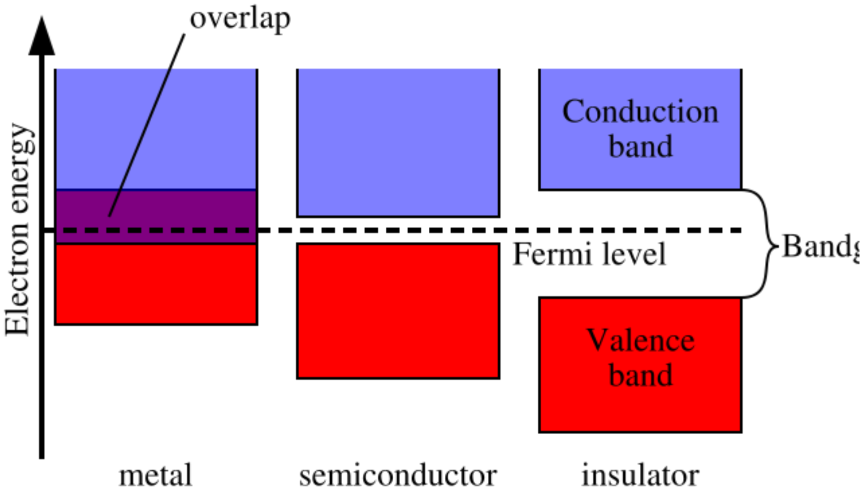
Transparency?

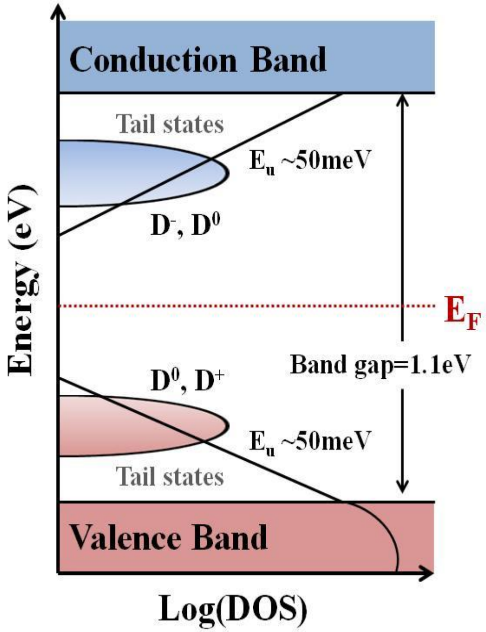
➔ Reflection, Absorption, Transmission

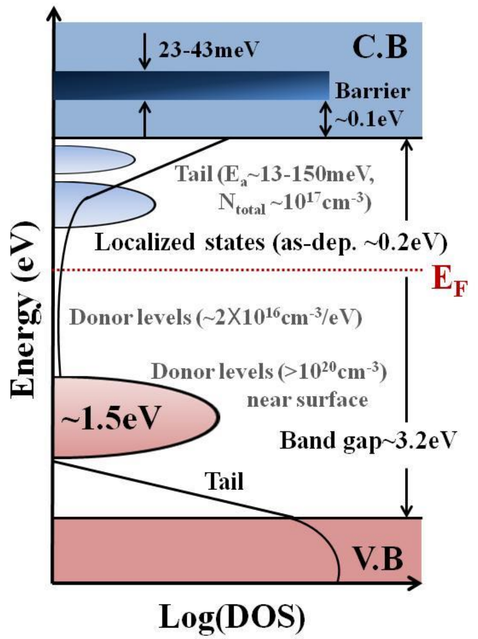
➔ Transmission of incident light ↑ (Visible light, 300nm ~800nm)

➔ Absorption of incident light ↓ (Bandgap < 3.5eV)

Semiconducting? Conducting?







- Semiconducting

➔ Region between conductor and insulator, Change of conductivity depending on conditions, Bandgap

- Conducting

➔ High conductivity, Free electrons, No bandgap

Transparent Conducting Oxides (TCO)

High transparency

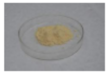
High mobility & High concentration (High conductivity)

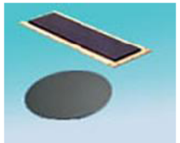
Low cost & Low Temp. & Large area

- Resistivity < 10^{-3} Ω·cm
- Sheet resistance < 10^{3} Ω/sq
- Transmittance > 80% (380nm~780nm visible range)
- Key components for FPD, Photovoltaic, Touch panels and Electronics
- Cost-efficient materials

1. CdO (1907)

2. In_2O_3 (1954, G. Rupprecht)





3. Impurity-doped binary compound

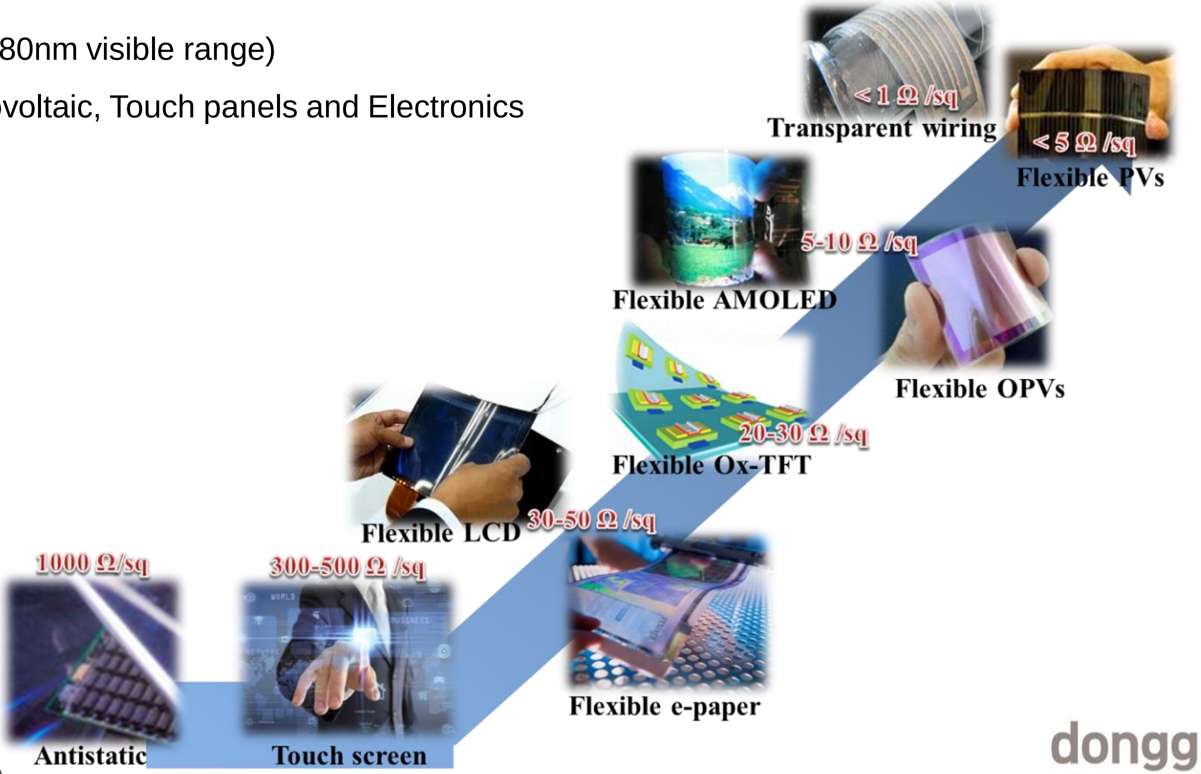
SnO_2 doped In_2O_3 : ITO (1968, van boort and groth)
F-doped SnO_2 :FTO
Sb_2O_5 doped SnO_2:ATO

4. 1990~2000: TCO films for specialized applications

Multicomponents oxide: combination of binary compound such as
Al-ZnO, Ga-ZnO, B-ZnO, CdO, Ga_3O_2, SnO_2, In_2O_3
Zn_2SnO_4, $MgIn_2O_4$, $CdSb_2O_6$:Y, ZnSnO, $GaInO_3$, $Zn_2In_2O_5$, $In_4Sn_3O_{12}$

5. 2000~ : New transparent conducting materials

PEDOT:PSS, CNT based electrode, Graphene, Grid, Indium free TCO



Issues

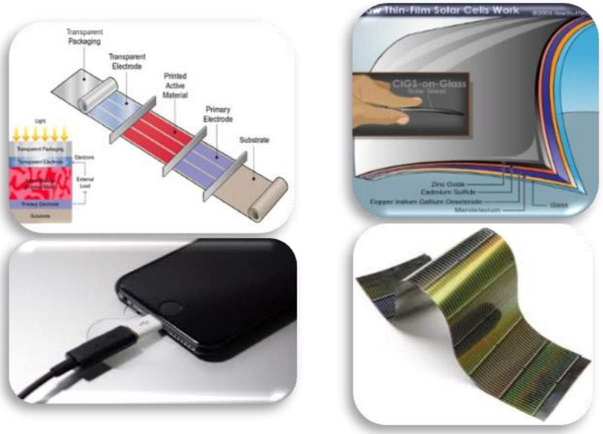
AMOLED

- **Resistivity: $10^{-4}\ \Omega\cdot$cm**
- **Sheet resistance: 1 Ω/sq**
- **Optical Transmittance: > 85%**
- **Work function: > 4.8 eV**
- **RMS roughness: 2nm**
- **Chemical stability**
- **Stability against humidity: 85°C, 85%**
- **Good wet etching**
- **Low cost element**

Touch Panel

- **High Transparency: >85%**
- **Sheet resistance: 400~500 Ω/sq**
- **Uniformity**
- **Reliability against temperature and moisture**
- **Haze properties**
- **Chemical and mechanical stability**
- **Continuous process**

Solar Cell



$$\eta_{EQE} = \eta_A\ \eta_{IQE} = \eta_A\ \eta_{ED}\ \eta_{CT}\ \eta_{cc}$$

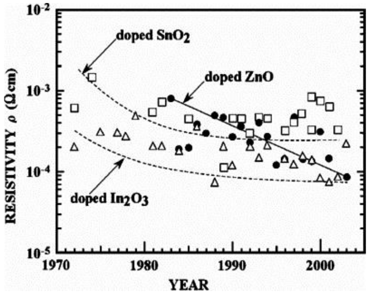
η_A : Photon absorption

η_{cc} : Collection of Carrier

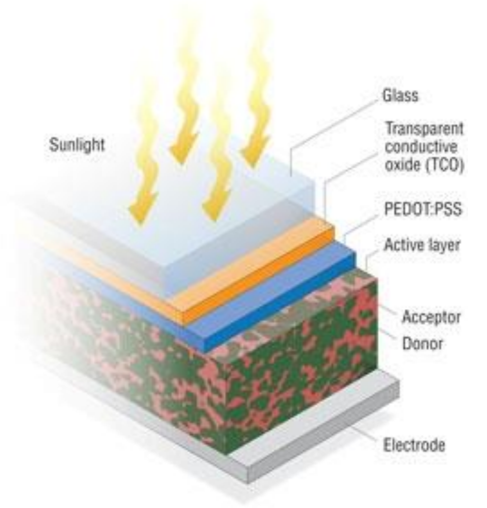
- **High Transparency: >85%**
- **Very low resistivity: ~ $10^{-4}\ \Omega\cdot$cm**
- **Smooth morphology**
- **Low cost (indium free-TCO)**
- **Superior flexibility**
- **Low temperature process**
- **Chemical stability against acid solution**
- **R2R based Large area coating technique**
- **Reliability**

Candidates of TCO

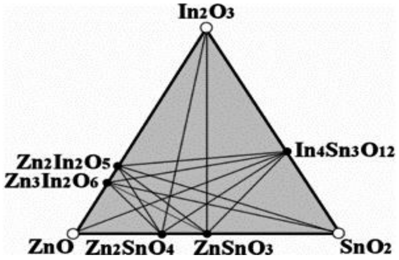
Indium free



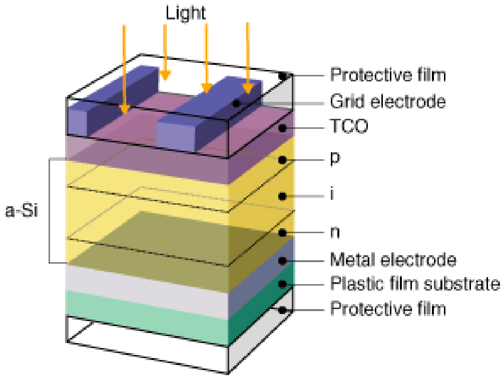
- ZnO, TiO, SnO_2 based TCO
- Al-ZnO, Ga-ZnO, B-ZnO, F-SnO2, Zn-SnO_2, Sb-SnO_2, Nb-TiO_2(NTO), Ta-TiO_2, Nb-Ta_2O_5



Indium reducing

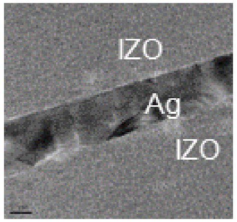


- Multicomponents TCO to reduce in composition
- InZnSnO (IZTO), InAlZnO, InAlSnZnO, InGaSnO, InGaZnO, TiInSnO (TITO)



Amorton Film Configuration

Multi-layered



- Oxide/Metal/Oxide
- ITO/Ag/ITO, IZO/Ag/IZO, IZTO/Ag/IZTO, GZO/Ag/GZO, AZO/Ag/AZO, NTO/Ag/NTO, BZO/Ag/BZO, TiO_2/Ag/TiO_2

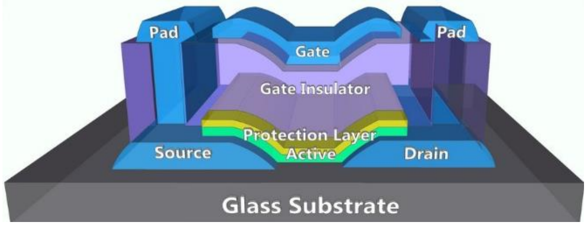
출처 : 2011 Displaybank 교육자료

Transparent Oxide Semiconductor

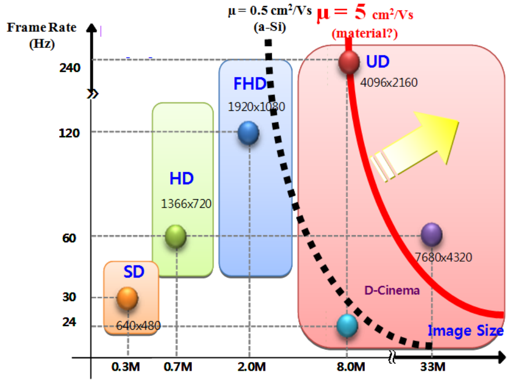
High transparency

High mobility & High concentration

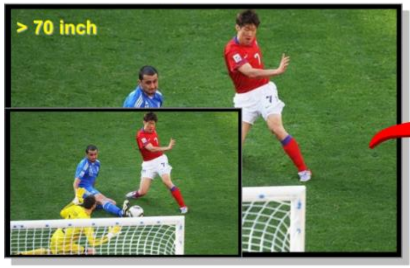
High quality & controllability (Density of State)



Channel layer for TFTs

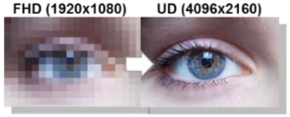


Large Area



High Resolution

FHD (1920x1080) UD (4096x2160)

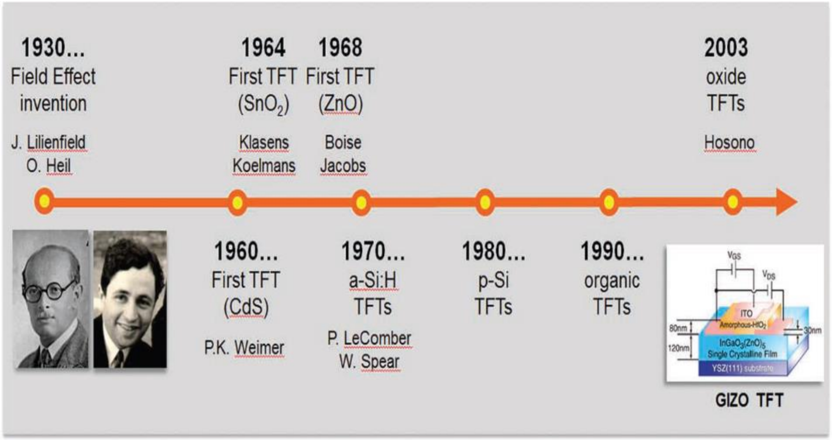


Fast Frame Rate

60, 120 Hz 240, 480 Hz

	a-Si TFT	poly-Si TFT	Oxide TFT
Semiconductor	Amorphous Si	Polycrystalline Si	Amorphous oxide
Transparency	No	No	Yes
TFT uniformity	Good	Poor	Good
Channel mobility	1 cm^2/Vs	~100 cm^2/Vs	10~100 cm^2/Vs
Pixel circuit	Simple (1T+1C)	Complex (5T+2C)	Simple (2T+1C)
Cost/Yield	Low/High	High/Low	Low/High
Process Temp.	~250˚C	>250˚C	RT~250˚C
ΔV_{th} (@I_{DS}=3μA)	>30V	<0.5V	~1.7V

History



1930…
Field Effect invention
J. Lilienfield
O. Heil

1960…
First TFT (CdS)
P.K. Weimer

1964
First TFT (SnO_2)
Klasens
Koelmans

1968
First TFT (ZnO)
Boise
Jacobs

1970…
a-Si:H TFTs
P. LeComber
W. Spear

1980…
p-Si TFTs

1990…
organic TFTs

2003
oxide TFTs
Hosono

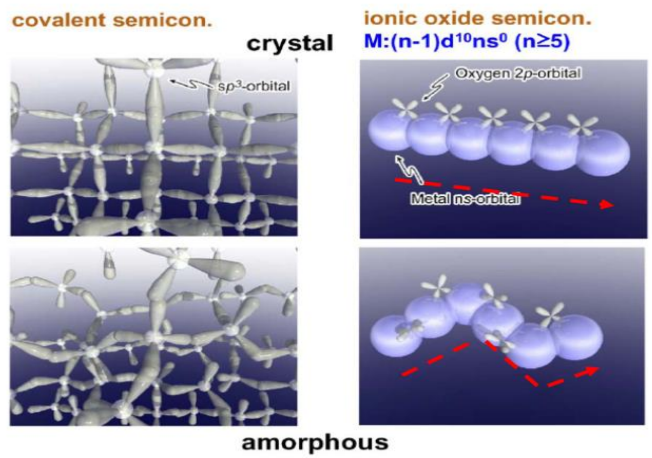
GIZO TFT

The Advantages

- *High Mobility (compared to a-Si)*
- *Room Temperature Deposition (Sputtering)*
- *Amorphous (no G.B. : Large Area Uniformity)*

Conduction Mechanism

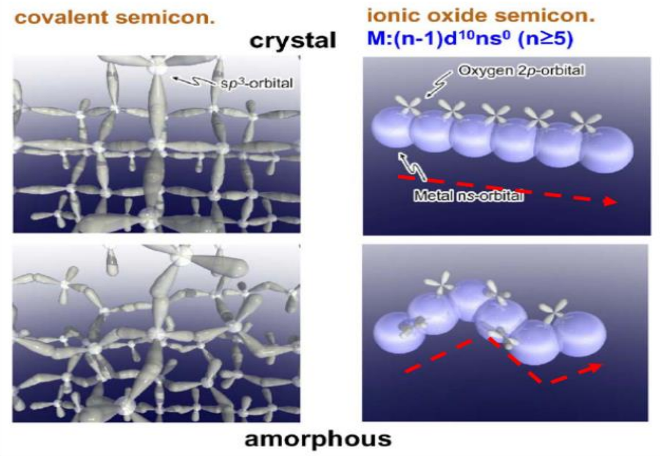
- *No Directionality*
- *Oxygen Deficiency – Carrier Generation*
- *Overlap of Vacant s Orbitals*
- *Ga-In-Zn-O (GIZO) is Best Known*



H. Hosono, *J. Non-Cryst. Solids* 352 (2006)

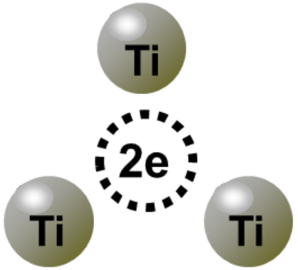
Oxygen vacancy

- **Conduction Mechanism**
  - *No Directionality*
  - *Oxygen Deficiency – Carrier Generation*
  - *Overlap of Vacant s Orbitals*
  - *Ga-In-Zn-O (GIZO) is Best Known*



H. Hosono, *J. Non-Cryst. Solids* 352 (2006)

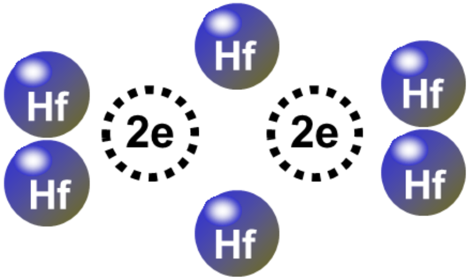
TiO_2 monovacancy



$Ti^{3+} \times 2 + Ti^{4+} \times 1 \rightarrow$

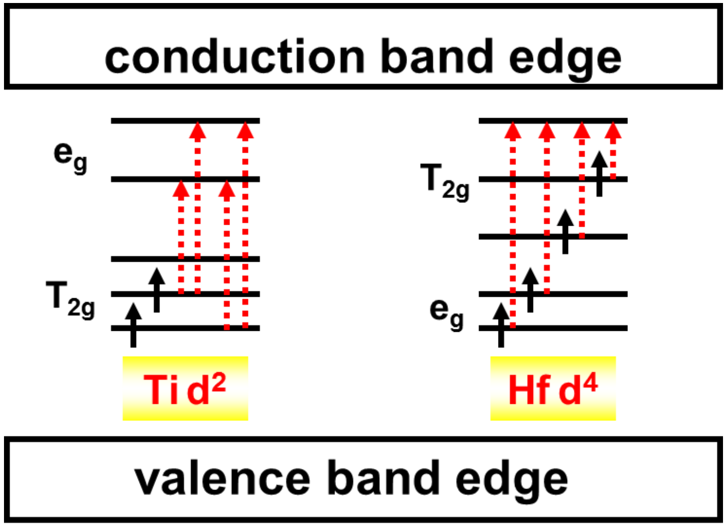
Ti d^2 configuration

HfO_2 divacancy



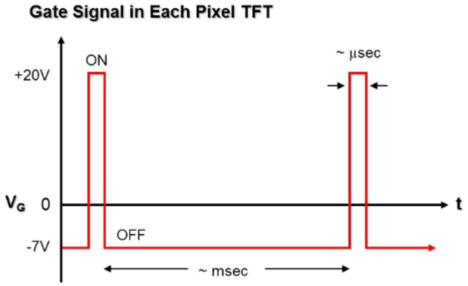
$Hf^{3+} \times 4 + Hf^{4+} \times 2 \rightarrow$

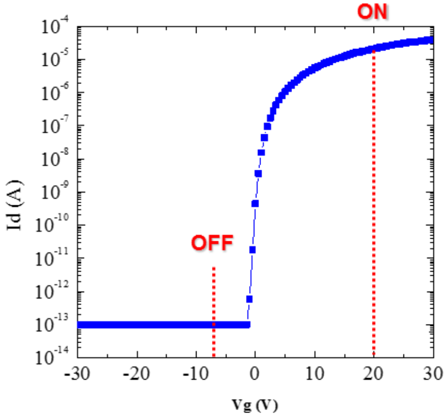
Hf d^4 configuration



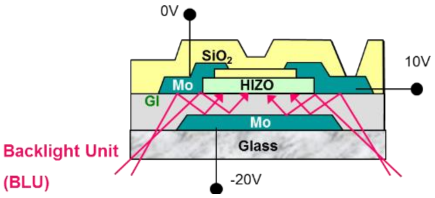
Issues

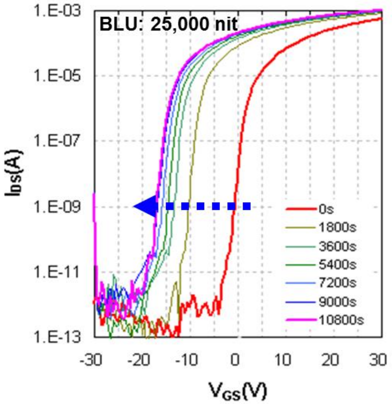
Bias Instability

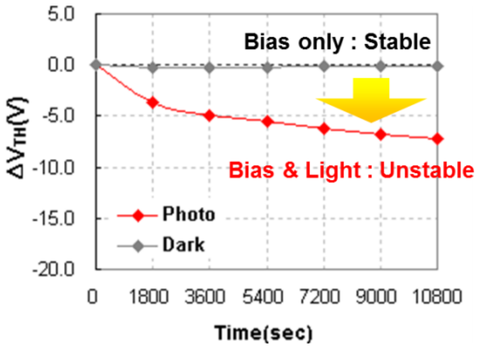




Ilumination Instability

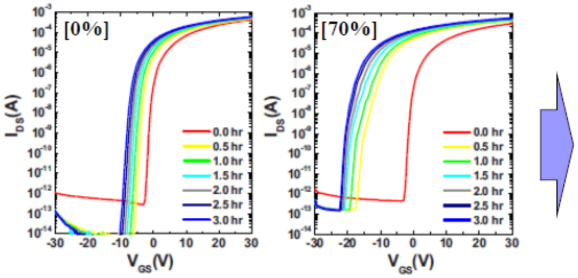


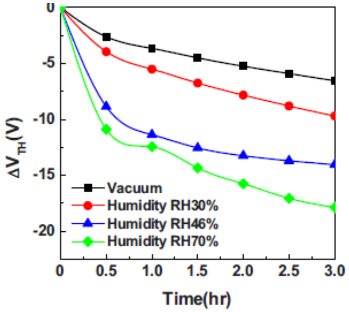




Environment Instability

Off-voltage Modulation	Air (after 20 days)	N_2 (after 20 days)
-7V		
-5V		
-3V		

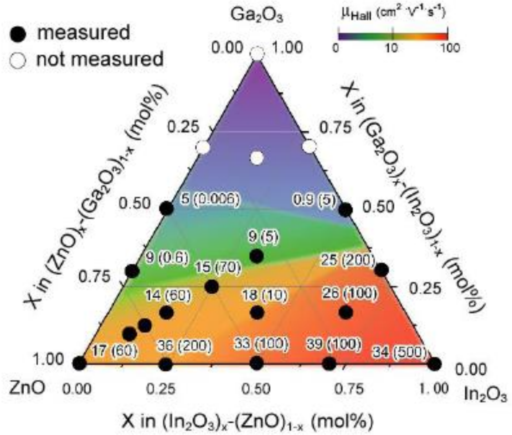


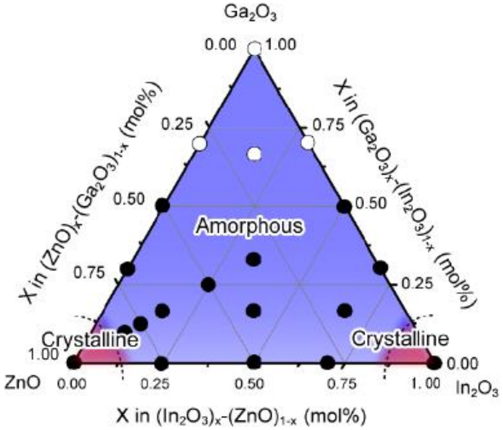


Candidates of TOS

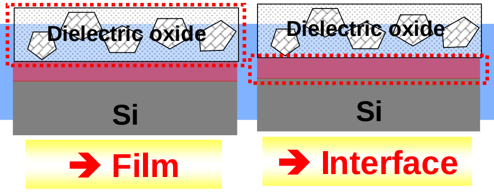
Material	Dopant or Compound
SnO_2	Sb, F, As, Nb, Ta
In_2O_3	Sn, Ge, Mo, F, Ti, Zr, Hf, Nb, Ta, W, Te
ZnO	Al, Ga, B, In, Y, Sc, F, V, Si, Ge, Ti, Zr, Hf
CdO	In, Sn
$ZnO-SnO_2$	Zn_2SnO_4, $ZnSnO_3$
$ZnO-In_2O_3$	$Zn_2In_2O_5$, $Zn_3In_2O_6$
$In_2O_3-SnO_2$	$In_4Sn_3O_{12}$
$CdO-SnO_2$	Cd_2SnO_4, $CdSnO_3$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

Channel Materials	Deposition Method	Mobility ($cm^2/V \cdot s$)	Subthreshold Swing (V/decade)	Process Temperature (°C)
a-ZnON	Reactive sputter	10	0.8	350
p-ZnON	ALD	6.7	0.67	150
MgZnO	MOCVD	40	0.25	450
a-InZnO	Sputter	20	1.2	R.T.
a-InZnO	Sputter	4.5	0.87	40
a-InZnO	Sputter	27 (19)	ND	600 (200)
a-InGaZnO	PLD	9	ND	R.T.
a-InGaZnO	Sputter	12	0.2	R.T.
a-InGaZnO	Sputter	35.9	0.59	350
ZrInZnO	Sputter	3.9	0.98	350
a-HfInZnO	Sputter	10	0.23	200
a-SnInZnO	Sputter	24.6	0.12	300
a-AlSnInZnO	Sputter	31.4	0.14	250
SiInZnO	Sputter	21.6	1.52	150
a-ZnSnO	Sputter	5–15 (20–50)	ND	300 (600)
a-ZnSnO	PLD	10	1.4	450
ZnSnO	Sputter	14	1.6	250
a-AlZnSnO	Sputter	10.1	0.6	180
GaZnSnO	Sputter	24.6	0.38	300
ZrZnSnO	Sputter	8.9	0.7	350





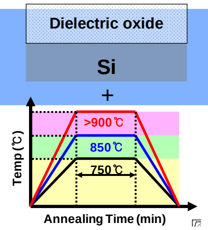
Characterization Issues



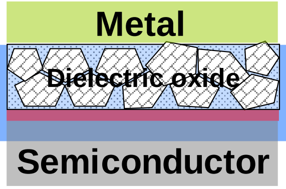
➔ Film

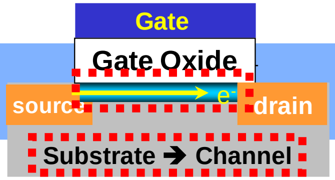
➔ Interface

Thermal Stability

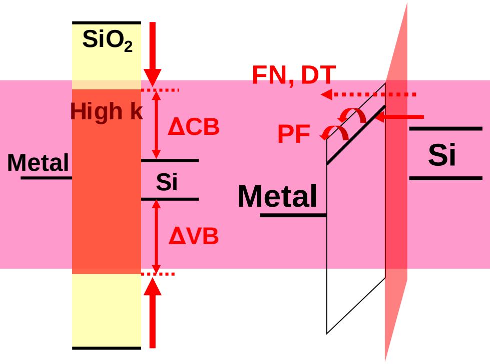


Physical Properties (cleaning, growth)

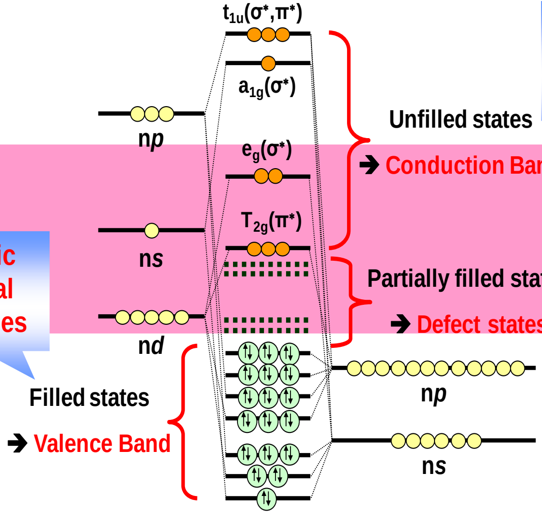




Electrical Properties (film, device)



Intrinsic Material Properties



Unfilled states

➔ Conduction Band

Partially filled states

➔ Defect states

Filled states

➔ Valence Band

Transport & Conduction mechanism

Reliability & Transport & Conduction mechanism

Electronic Structure (Band Structure, Atomic Configuration, Defects)

➔ Importance of understanding for electronic structure

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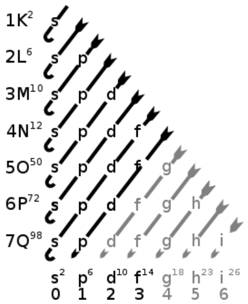
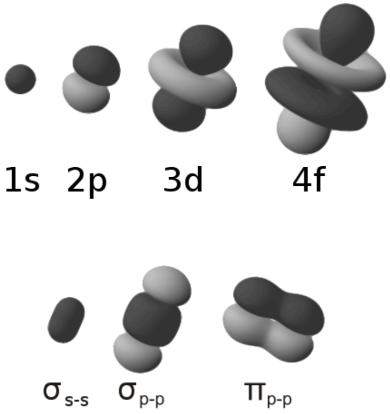
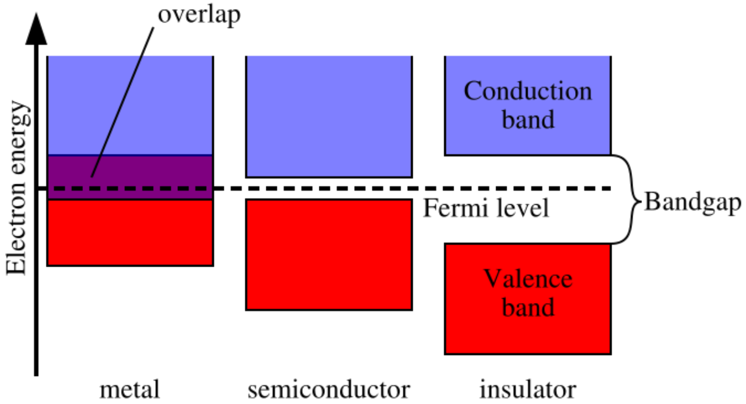
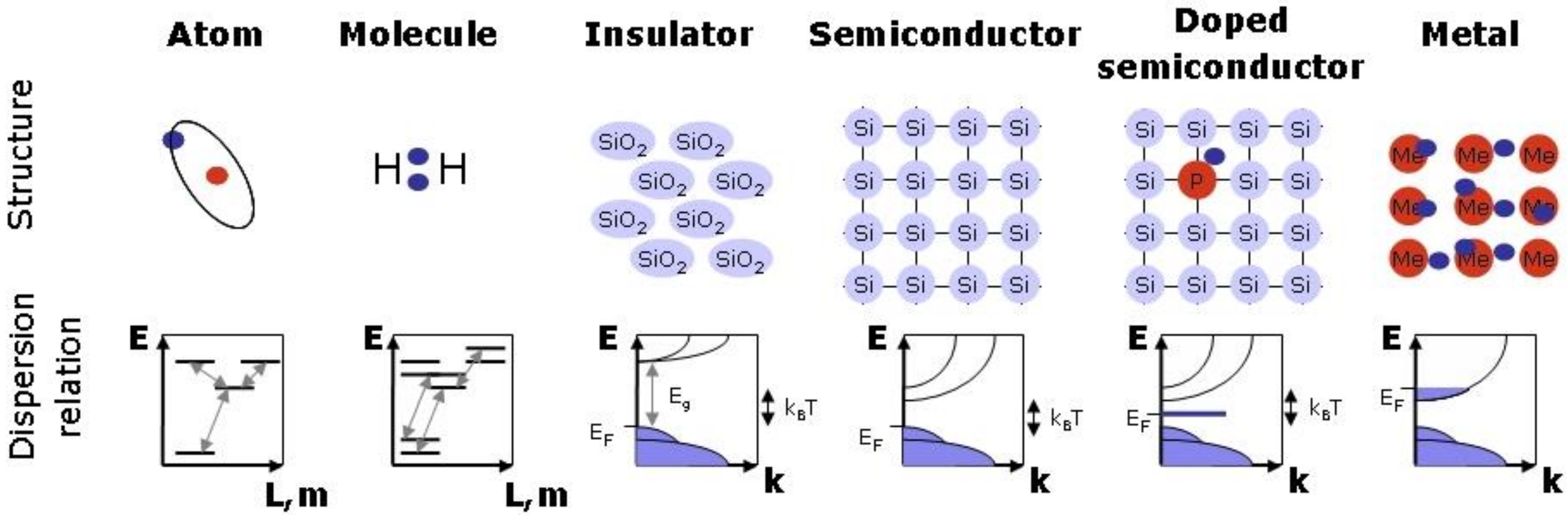
Importance of electronic structure





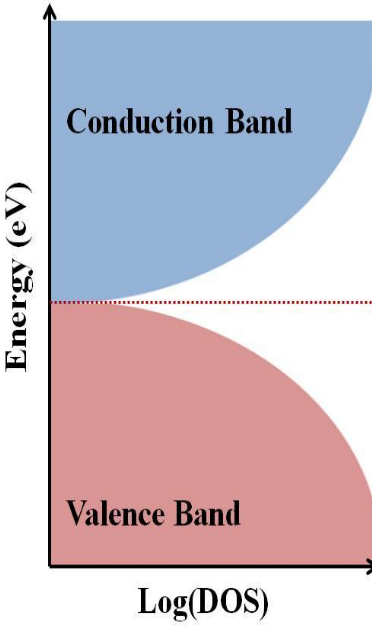
$1s^{2}_{2}2s^{2}_{4}2p^{6}_{10}3s^{2}_{12}3p^{6}_{18}4s^{2}_{20}3d^{10}_{30}4p^{6}_{36}5s^{2}_{38}4d^{10}_{48}5p^{6}_{54}6s^{2}_{56}4f^{14}_{70}5d^{10}_{80}6p^{6}_{86}7s^{2}_{88}5f^{14}_{102}6d^{10}_{112}7p^{6}_{118}$



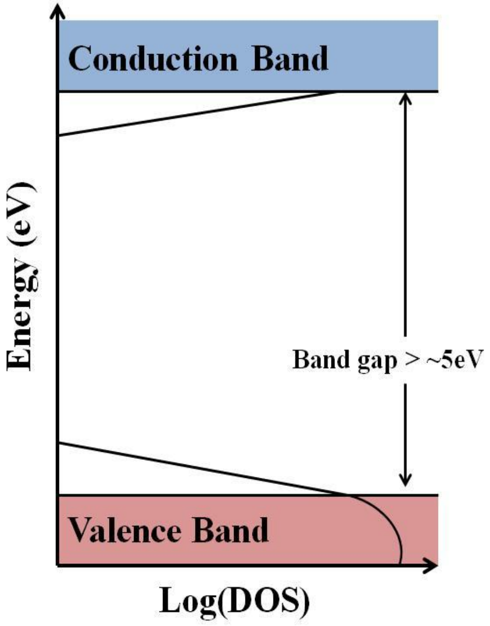


Answers how the electrons behave in matter. ➔ **Intrinsic material property, conducting & transport mechanism, reliability**

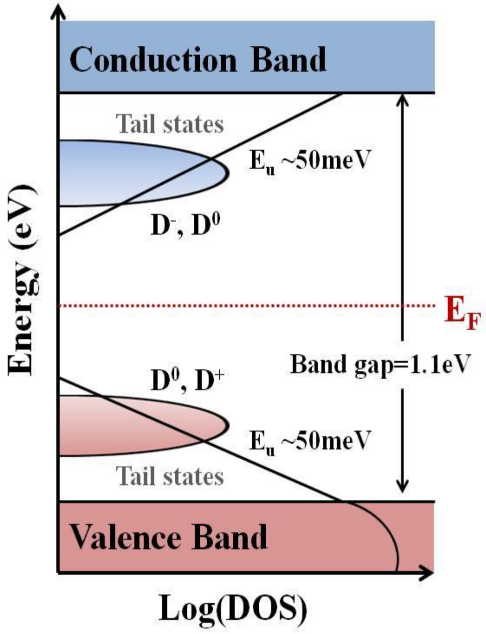
Electronic Structures of Solid



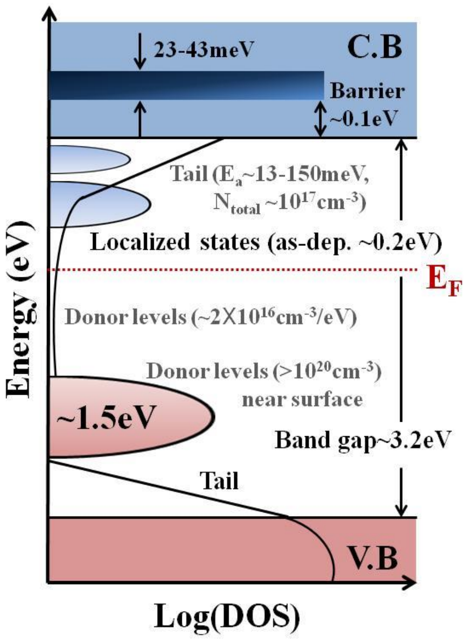
[Metal DOS model]



[Insulator DOS model]



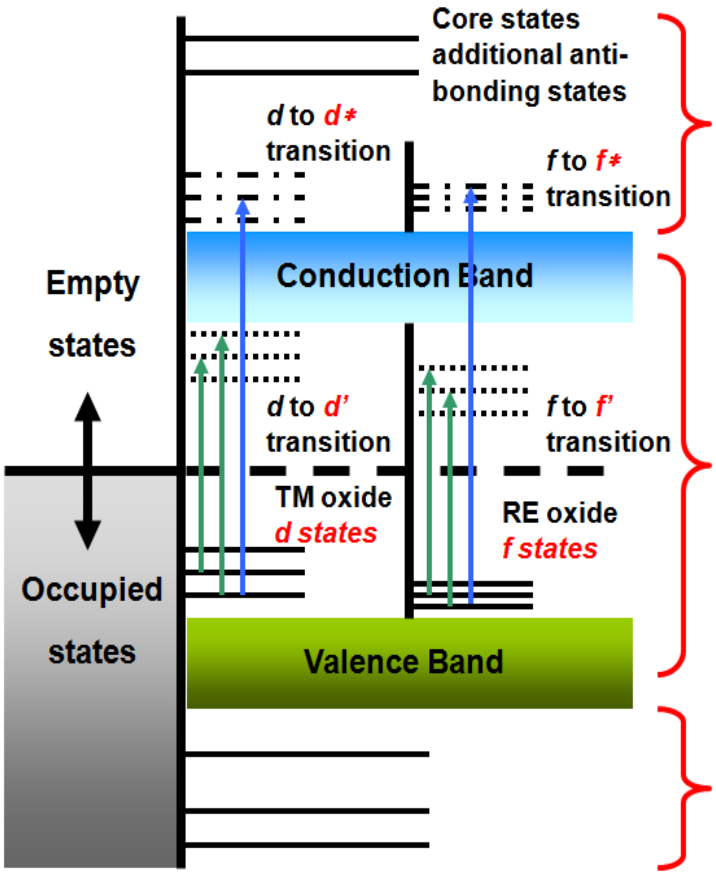
[a-silicon DOS model]



[a-IGZO DOS model]

➔ ***Importance of understanding for Electronic Structure!!***

Analysis of Electronic Structure



Virtual bound state regime

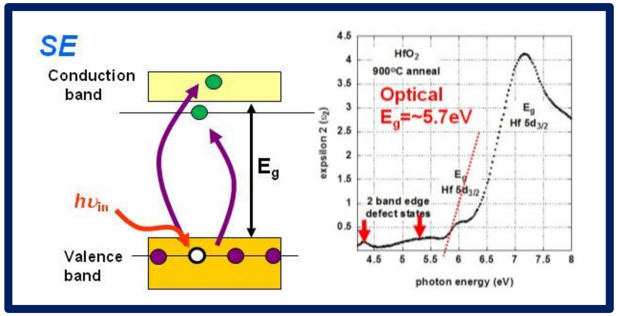
X-ray Absorption Spectroscopy (XAS)

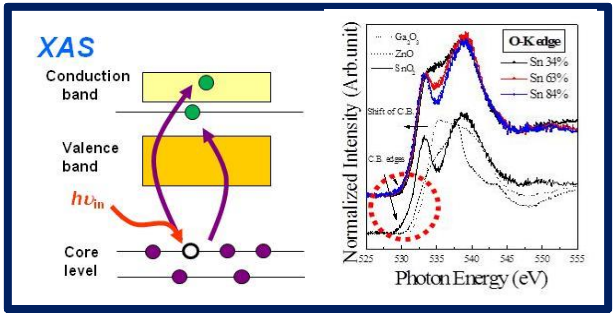
Pre-edge regime

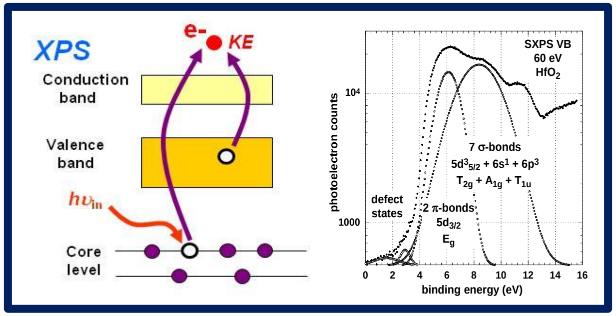
XAS & Spectroscopic Ellipsometry (SE) & X-ray Photoelectron Spectroscopy (XPS)

Shallow and deep core regime

XPS & X-ray Emission Spectroscopy (XES)







Spectroscopic analysis by SE, XAS, XPS, XES in PAL, SSRL, PF

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- Transparent Oxide Semiconductors (TOS)

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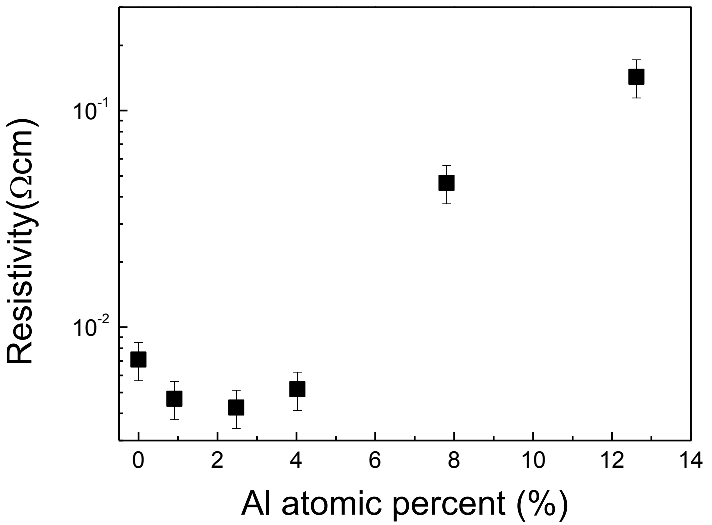
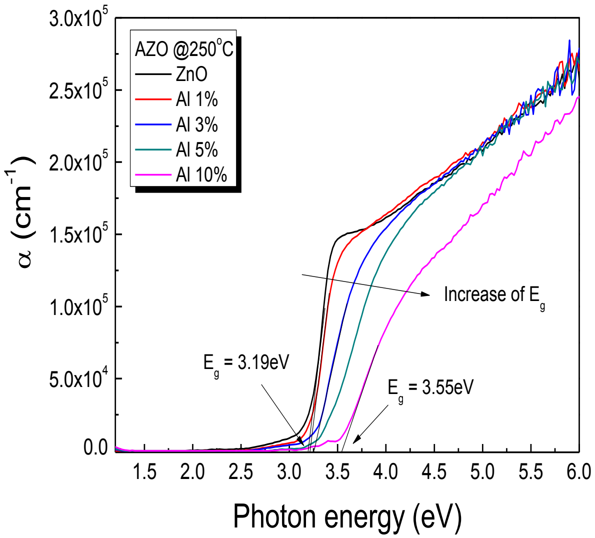
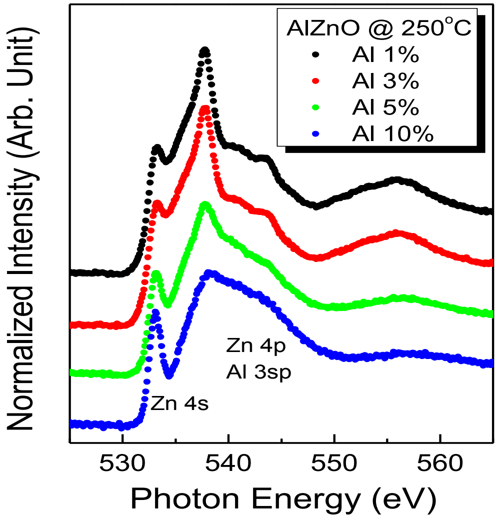
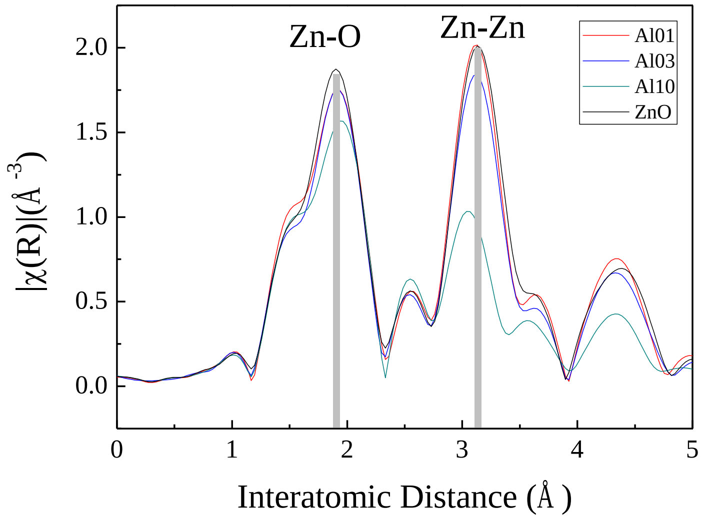
Applications

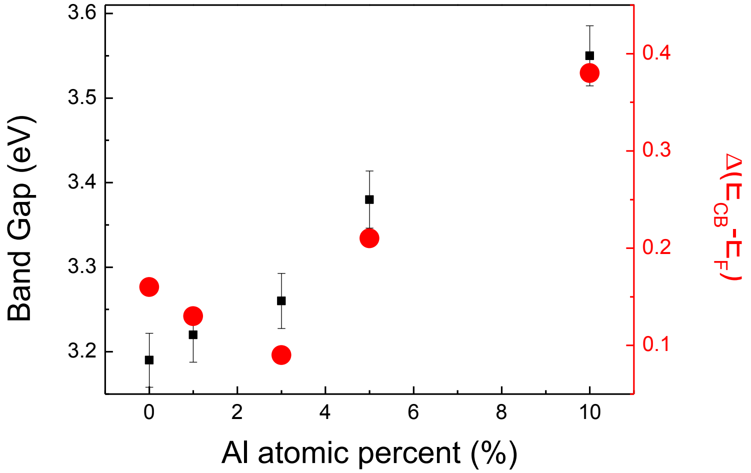
AlZnO





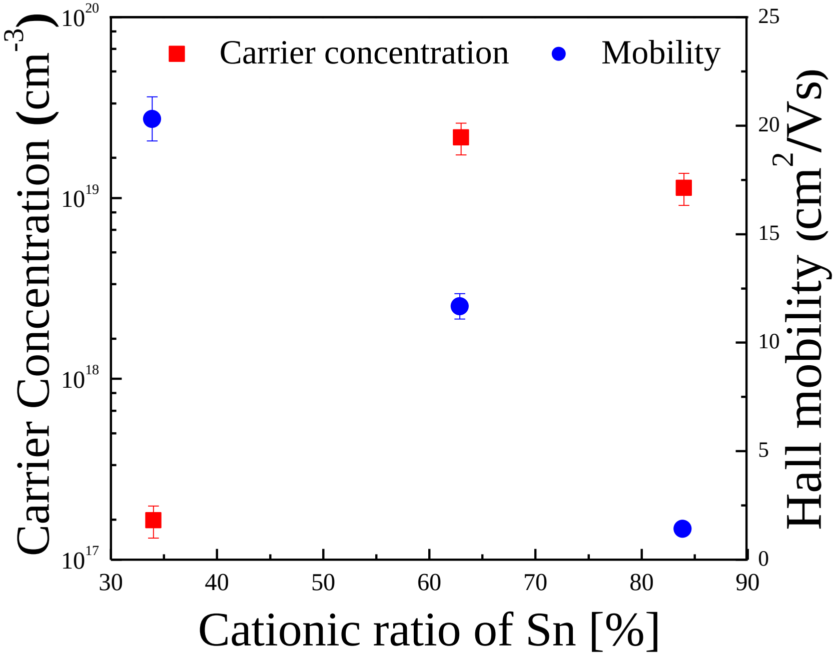


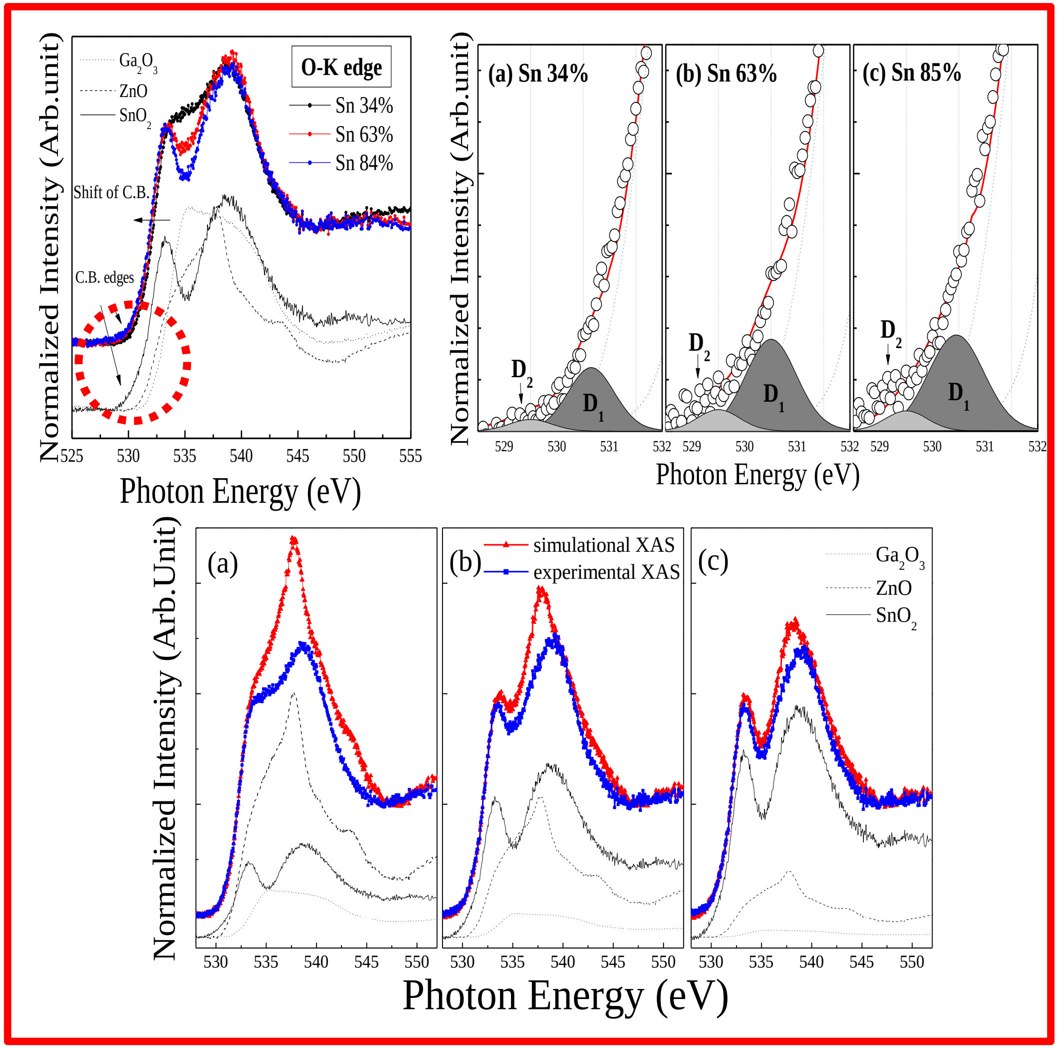




➔Relation between electrical property and electronic structure (conduction band & bandgap & band offset) ***Chung et. al. CI 41, 1641 (2015)***

GaZnSnO





➔Relation between electrical property and electronic structure (band edge & electronic structural boundary)

Chung et. al. APL 104, 182106 (2014)

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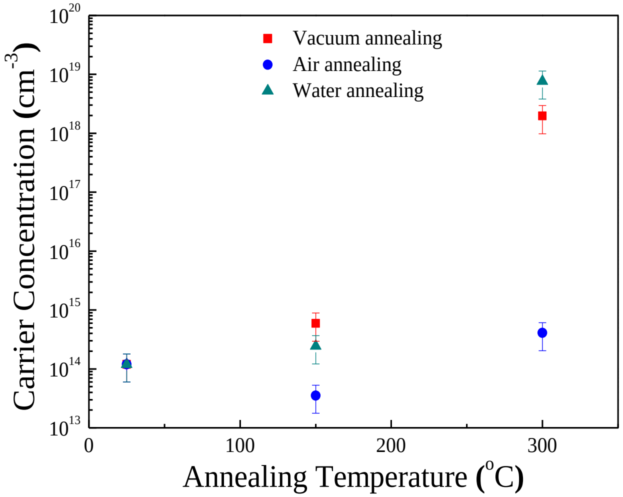
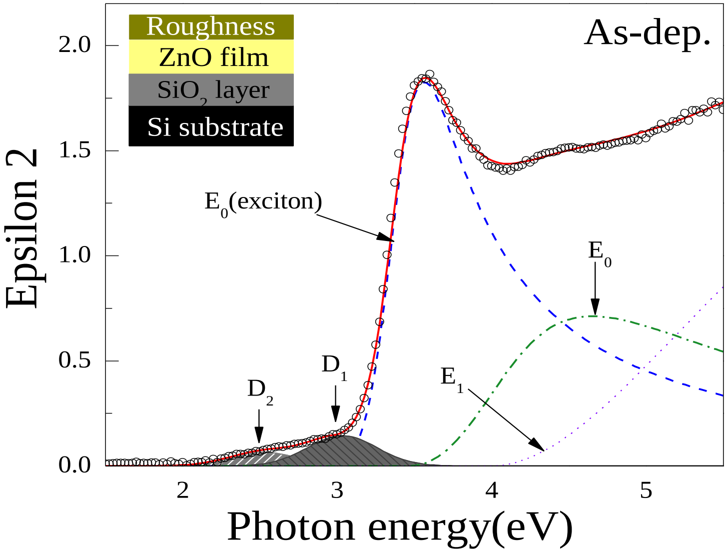
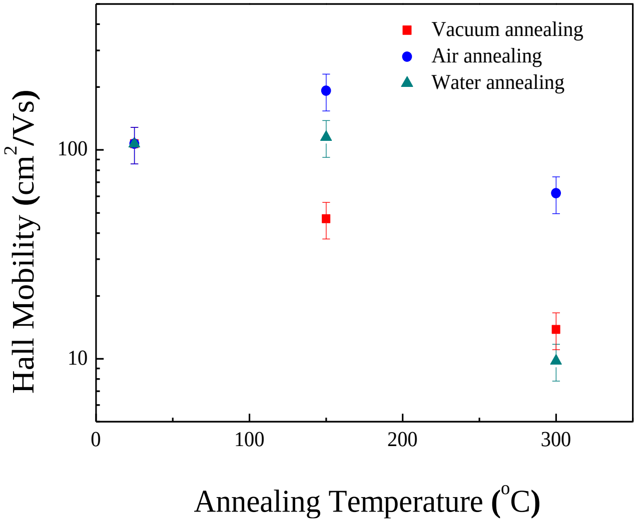
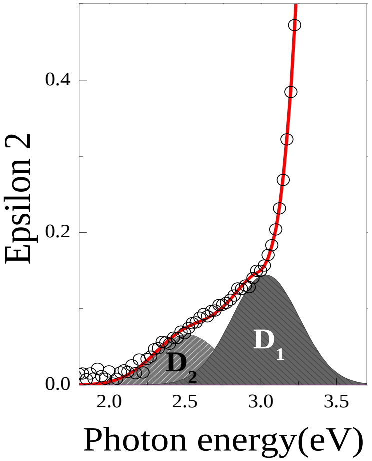
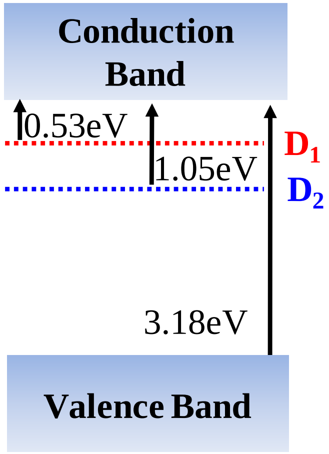
ZnO by thermal treatments











Conduction Band

0.53eV

1.05eV

D$_1$

D$_2$

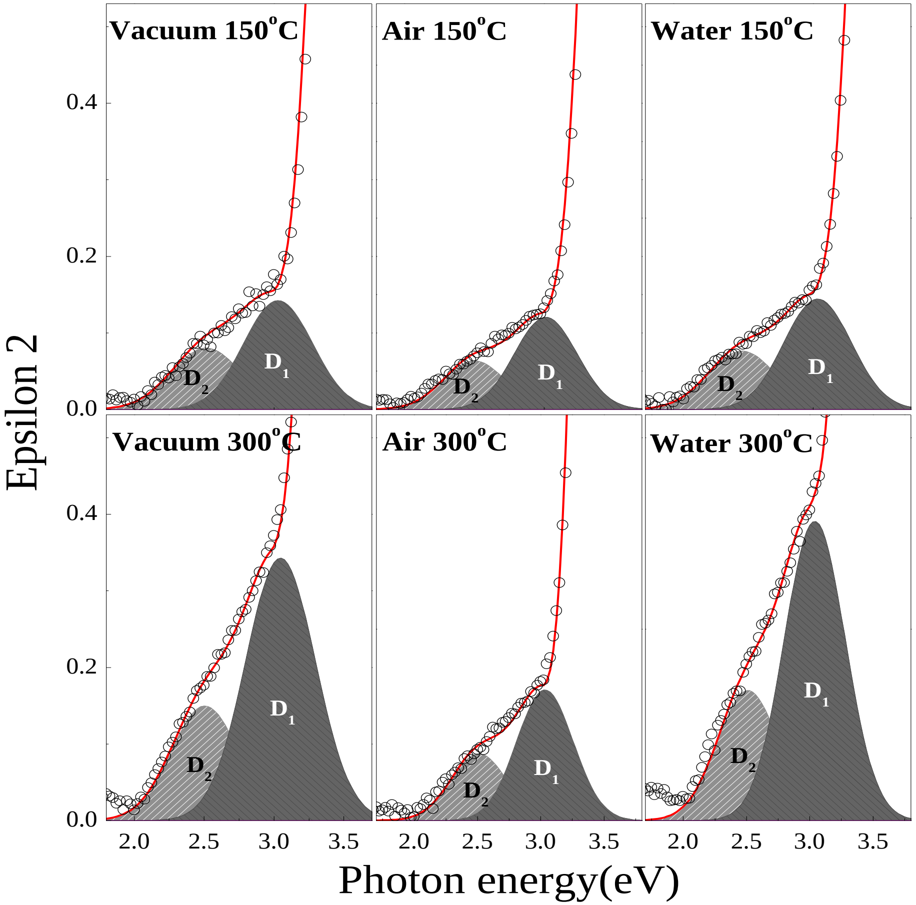
3.18eV

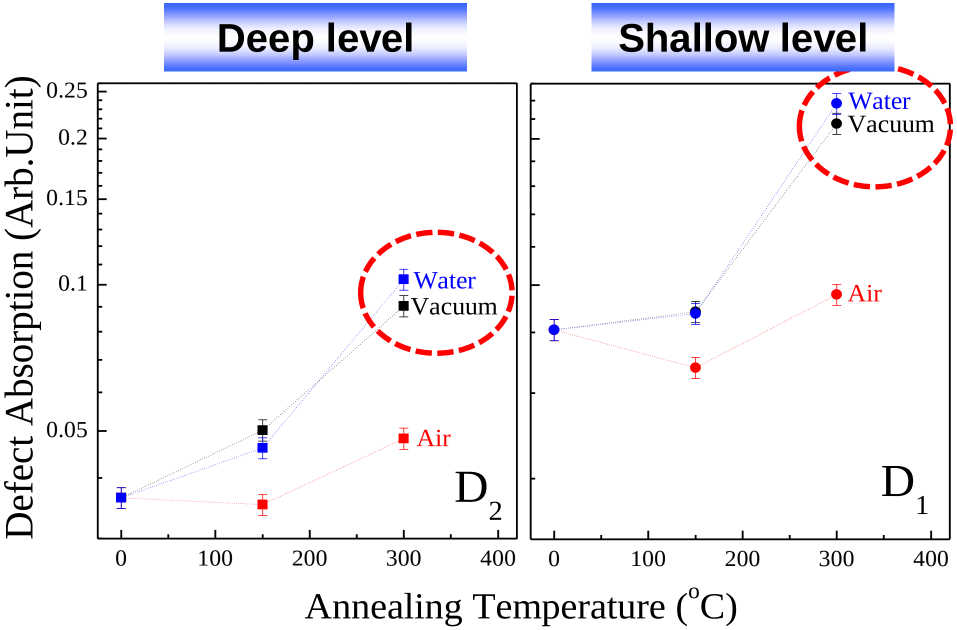
Valence Band

→ Changes of electrical properties by thermal treatments

Chung et. al. ESL 15, H133 (2012)

ZnO by thermal treatments





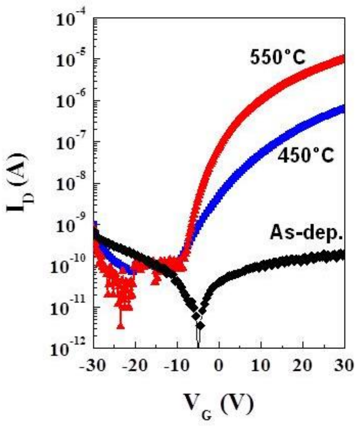
$$V_o \rightarrow V_o^{2+} + 2e^-$$

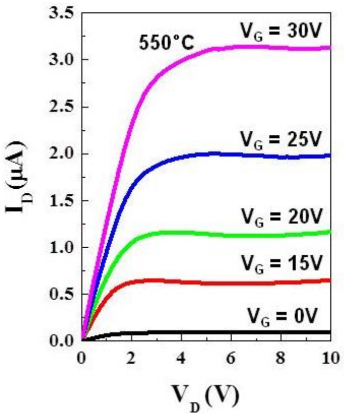
➔*Deep level : mobility*

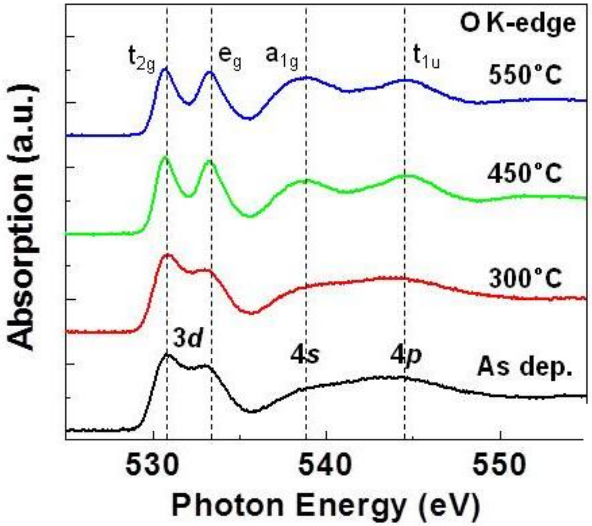
➔*Shallow level : carrier concentration*

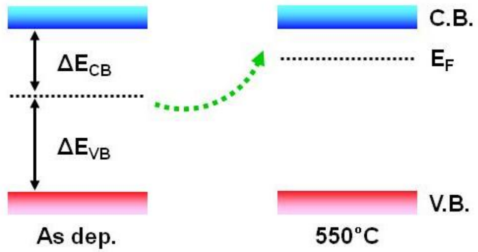
Chung et. al. ESL 15, H133 (2012)

TiO_{2-x} TFT

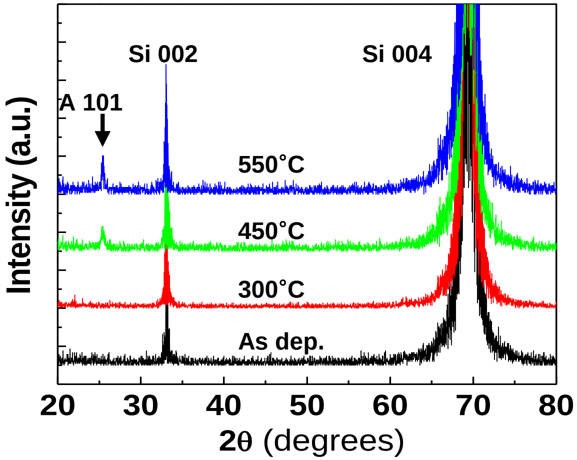








	E_g (eV)	ΔE_{VB} (eV)	ΔE_{CB} (eV)
As dep.	3.64	2.84	0.80
550°C	3.62	3.02	0.60



➔Device operation of TiO_{2-x} annealed above 450°C

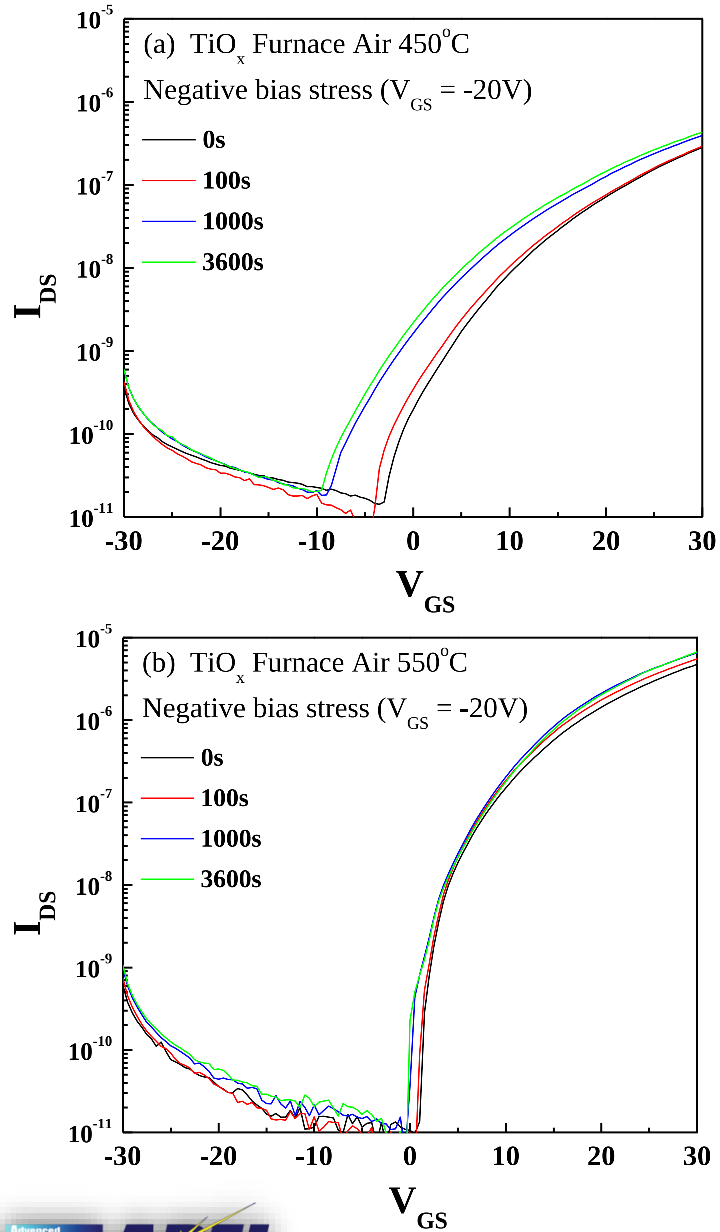
➔ Anatase structure

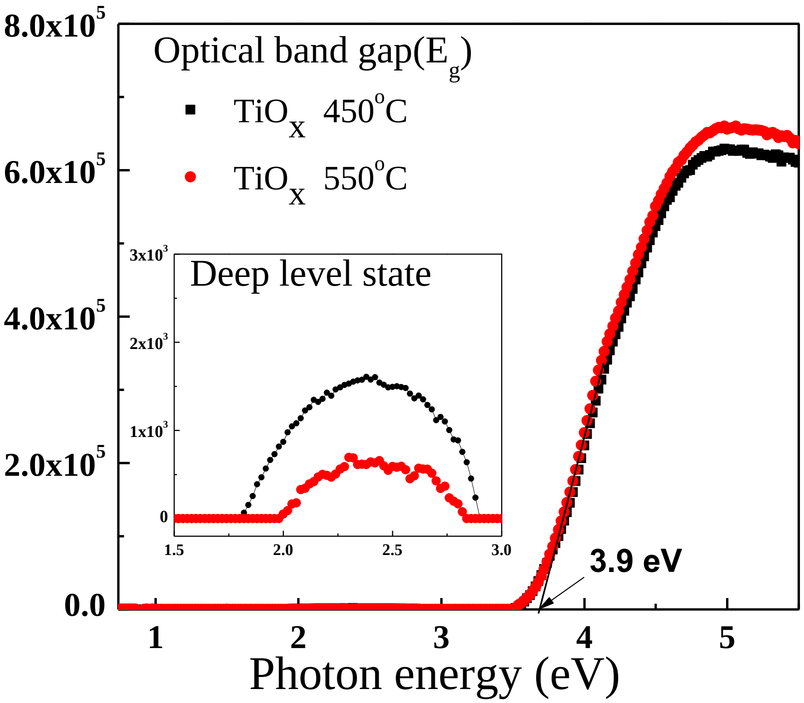
➔ Changes in molecular orbital ordering

➔ Decrease of conduction band offset

Chung et. al. APL 99, 142104 (2011)

TiO_{2-x} reliability

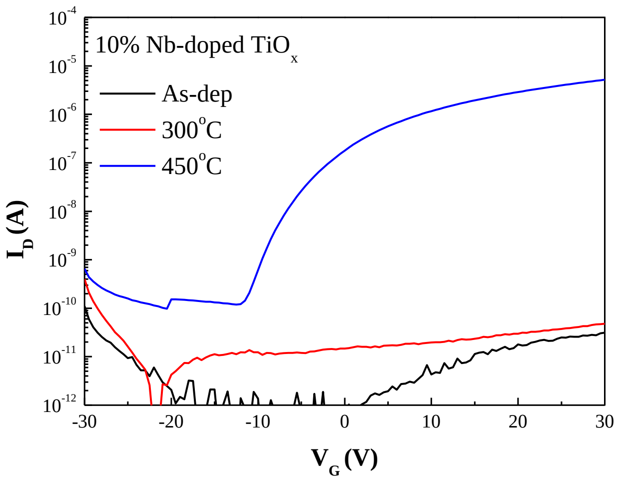


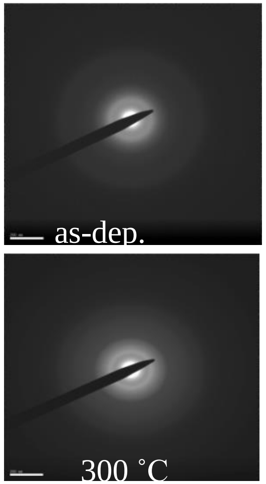


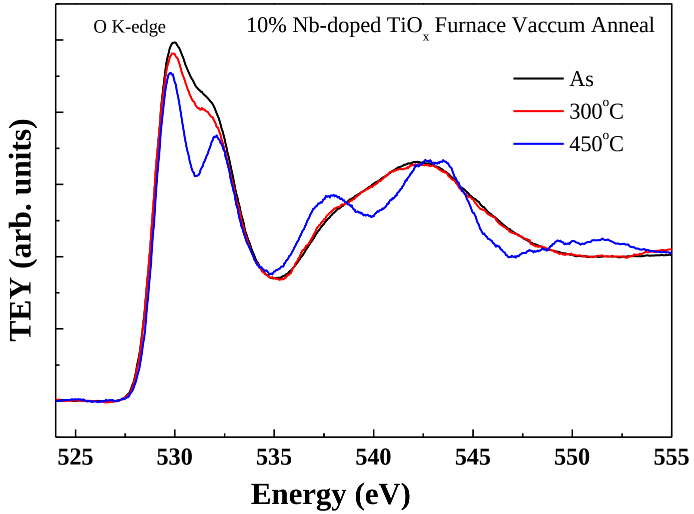
➔Relation between device reliability and band edge state

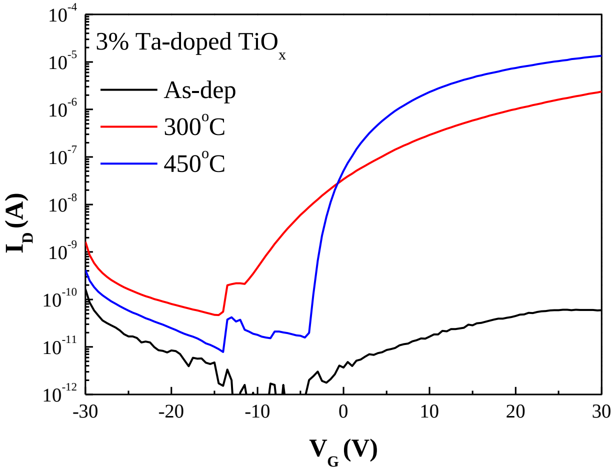
Chung et. al. JVST-B 31, 021204 (2013)

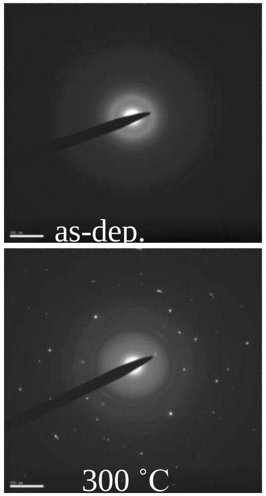
Nb or Ta-doped TiO_{2-x} TFT

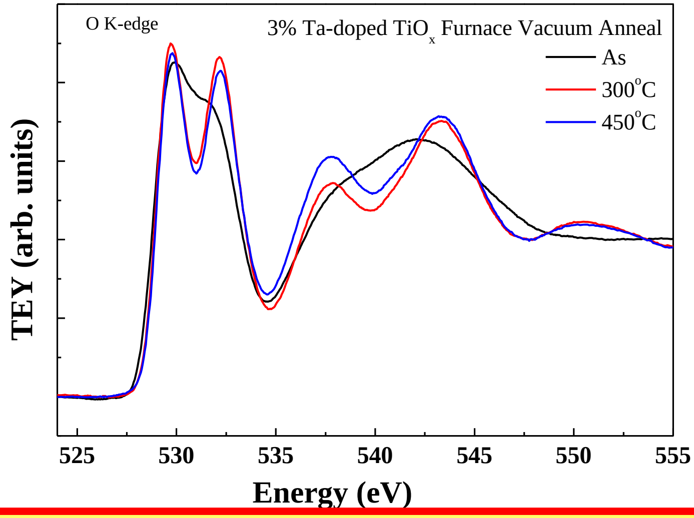










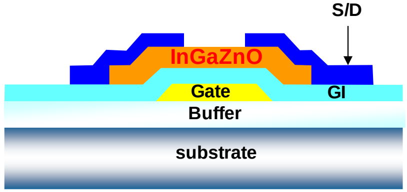


➔ ***Device operation at lower temperature (300°C)***

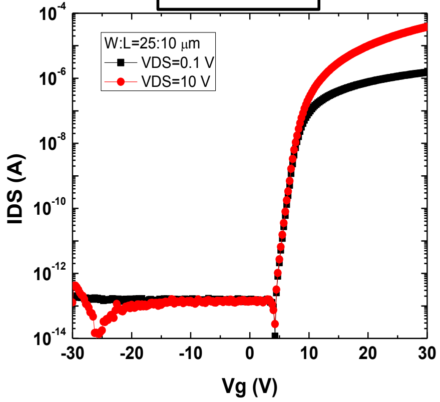
➔ ***Ordering of MO structure of Ta doped TiO_{2-x}***

Chung et. al. APL 103, 213501 (2013)

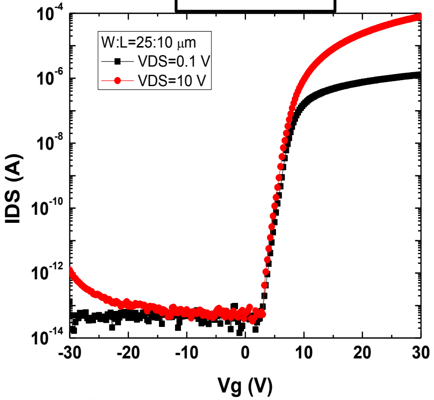
InGaZnO TFT



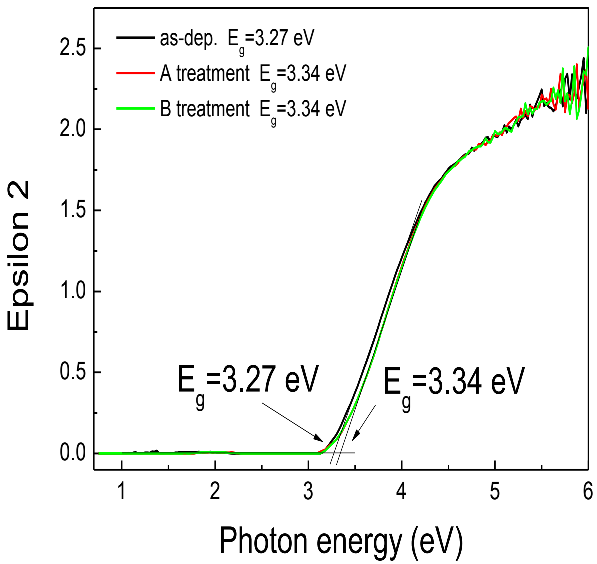
A treatment

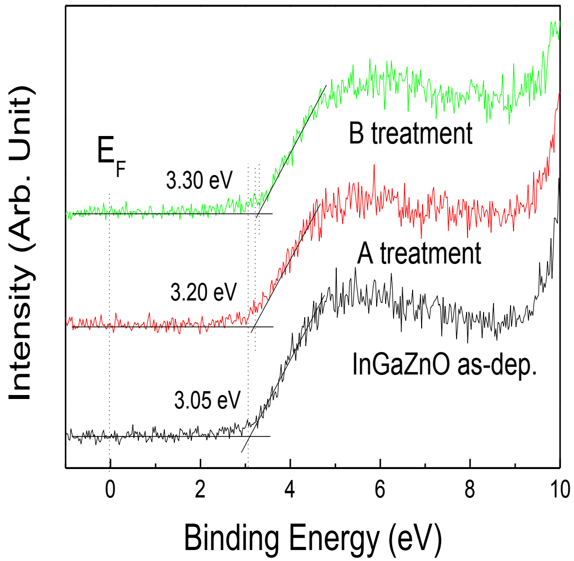


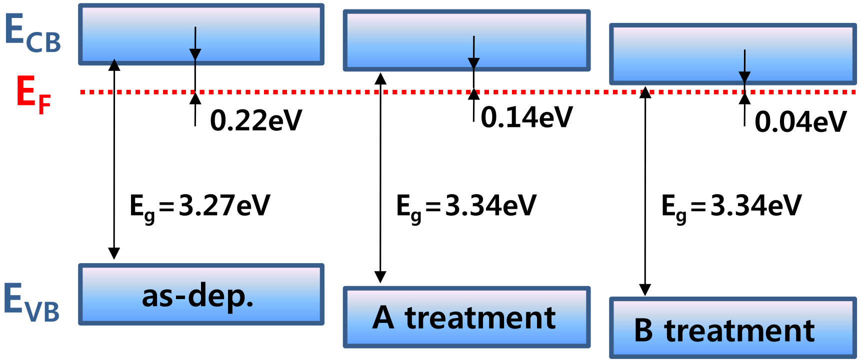
B treatment



Single	Ion	Ioff	Mobility	Vth@1nA	S.S
A treatment	4.06E-05	8.05E-14	6.65	6.00	0.71
B treatment	8.09E-05	1.39E-14	11.32	5.00	



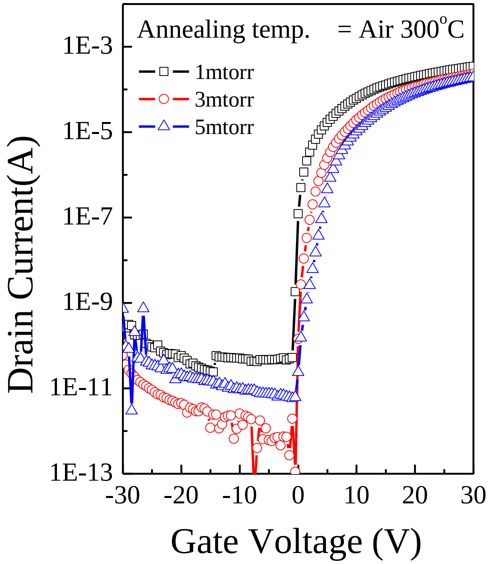


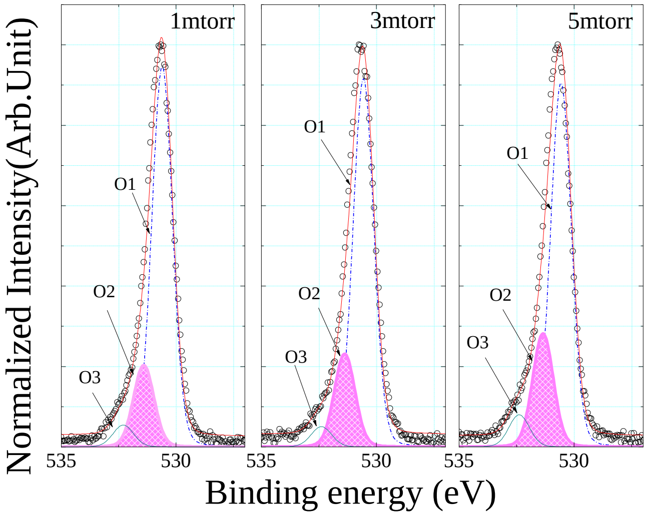


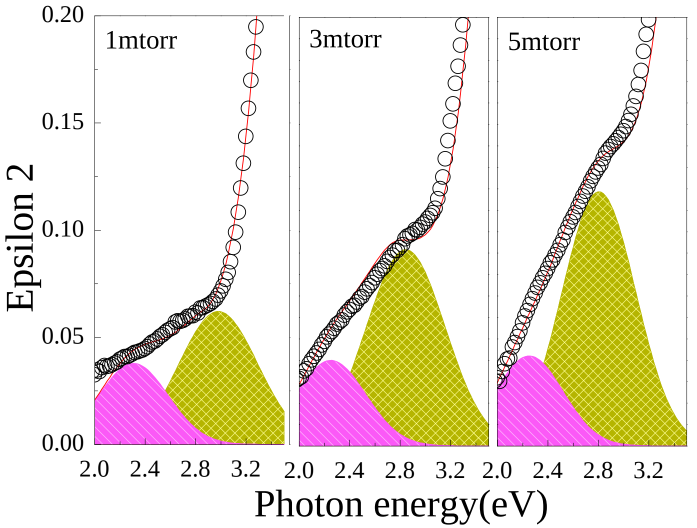
➔Relation between device performance and band alignment

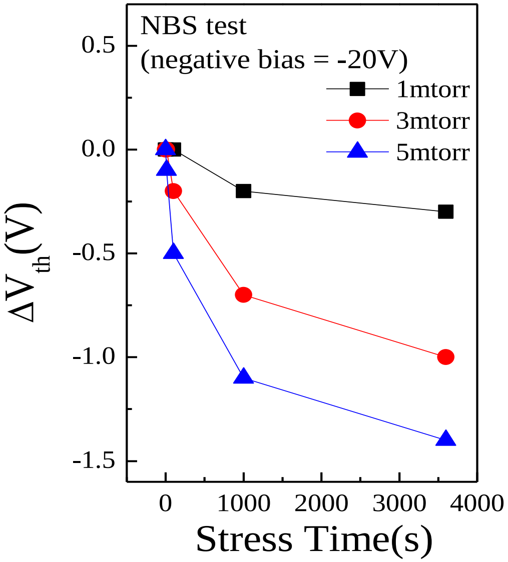
Chung et. al. JPD 45, 415307 (2012)

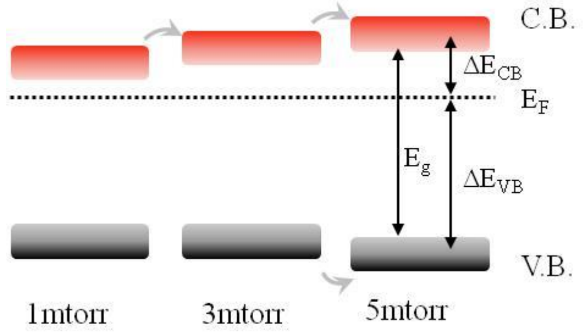
TaInZnO TFT (Process pressure)

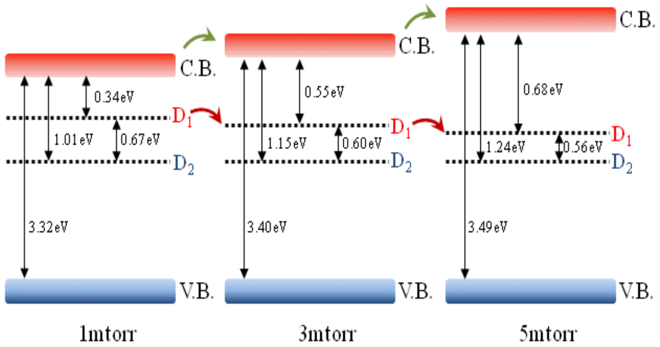








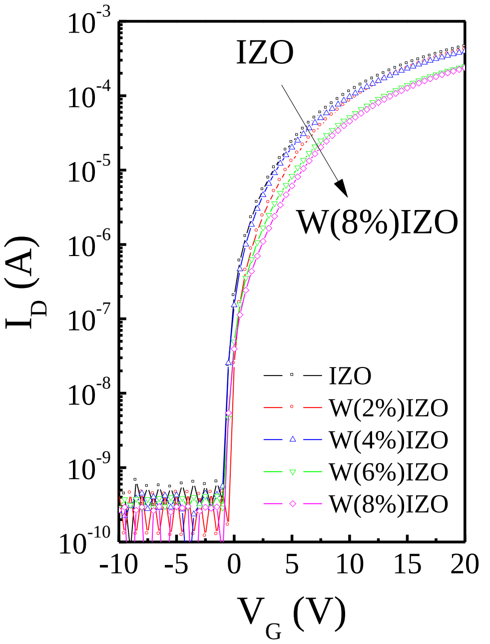


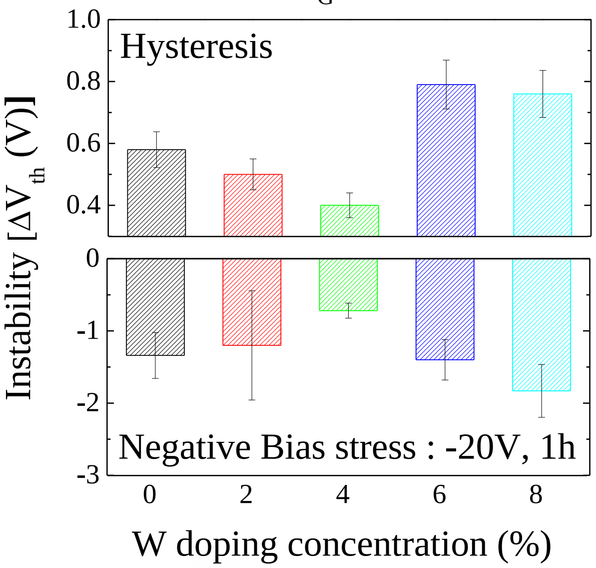


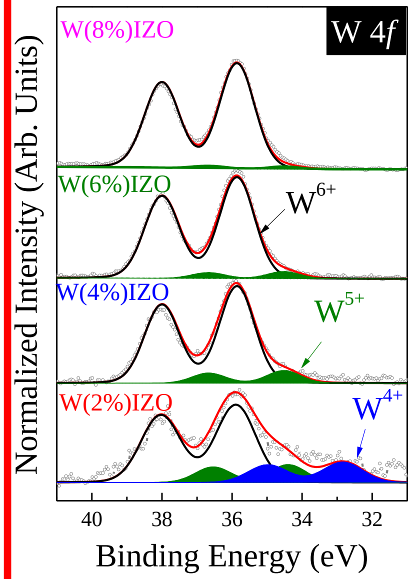
➔Relation between device performance, stability and vacancies, band edge states, band alignment

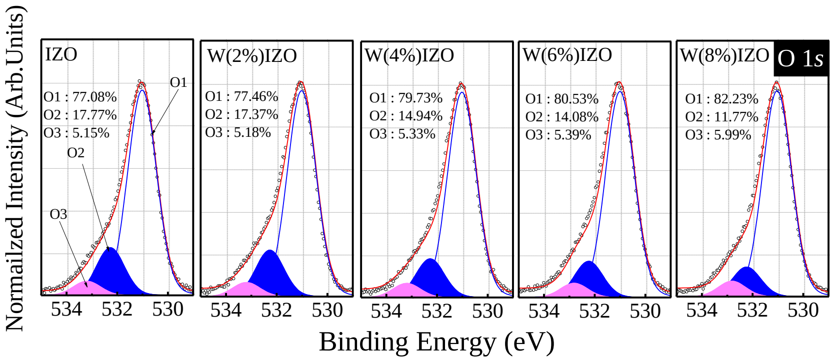
Chung et.al. APL 102, 102102 (2013)

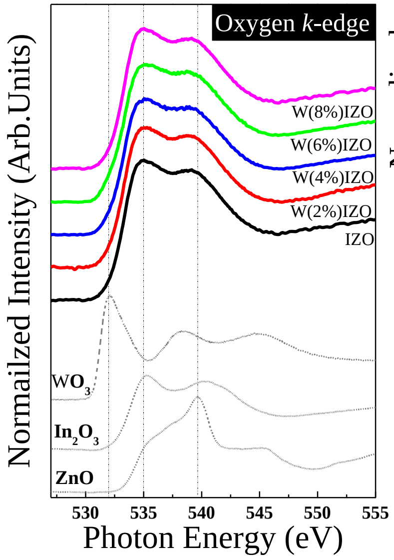
WInZnO TFT (W concentration)

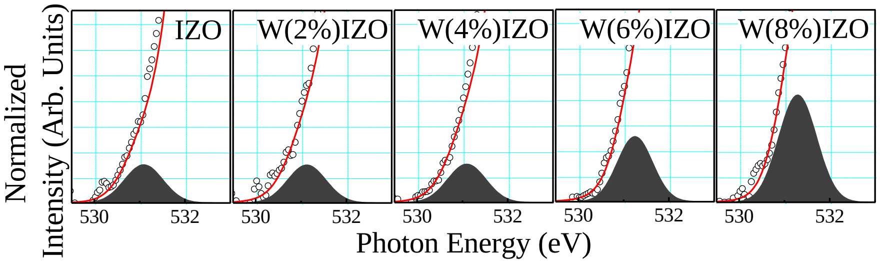






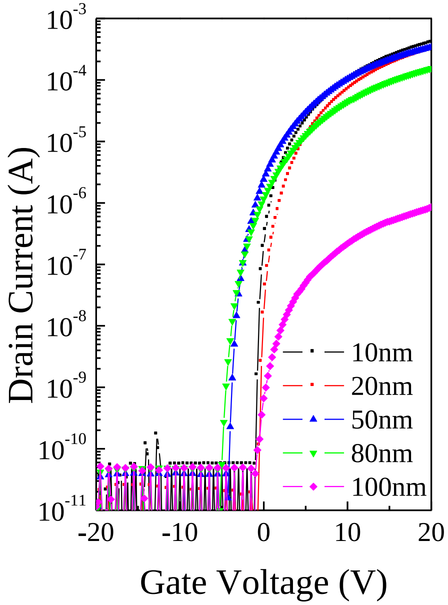


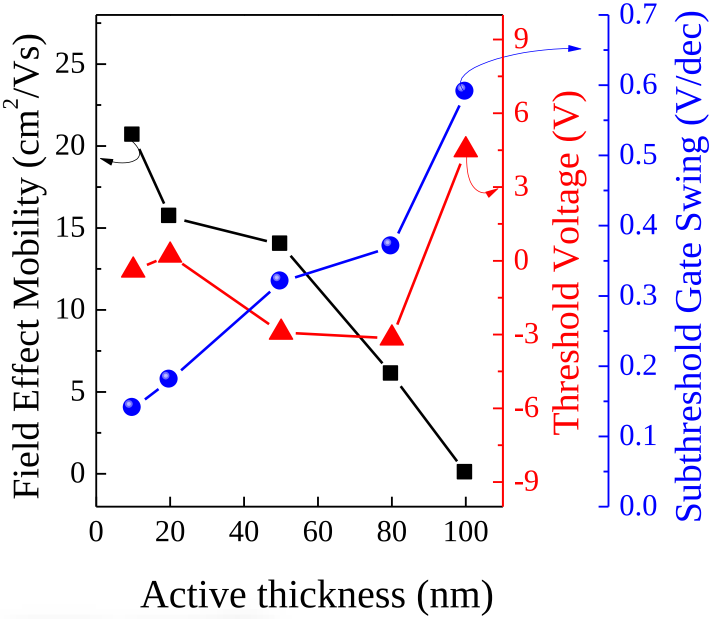


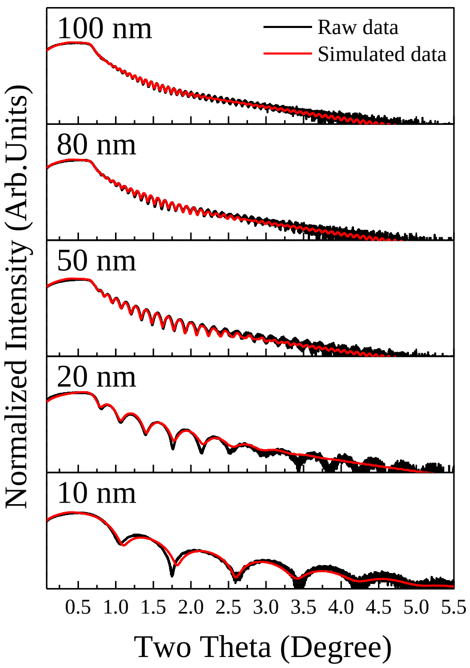


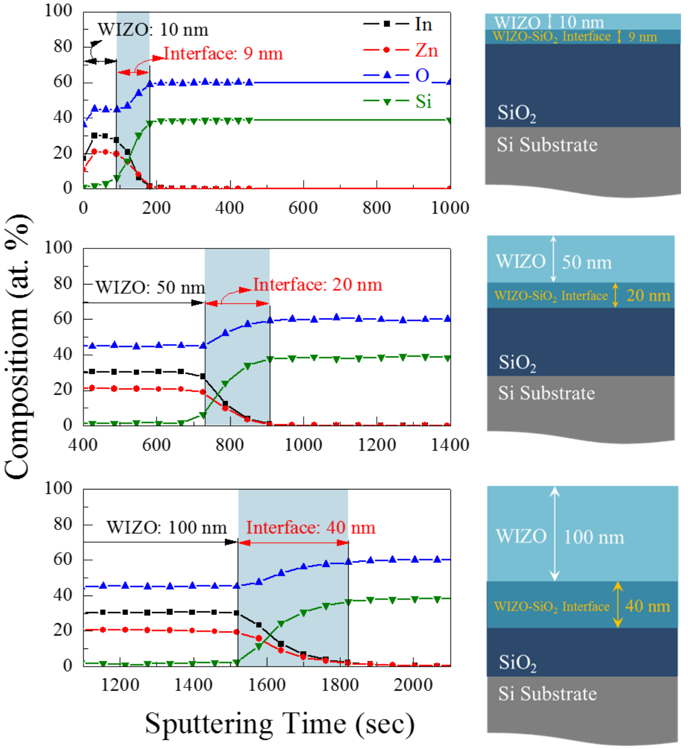
➔The role of carrier controller is important for improving the stability of the oxide TFTs

WInZnO TFT (active layer thickness)





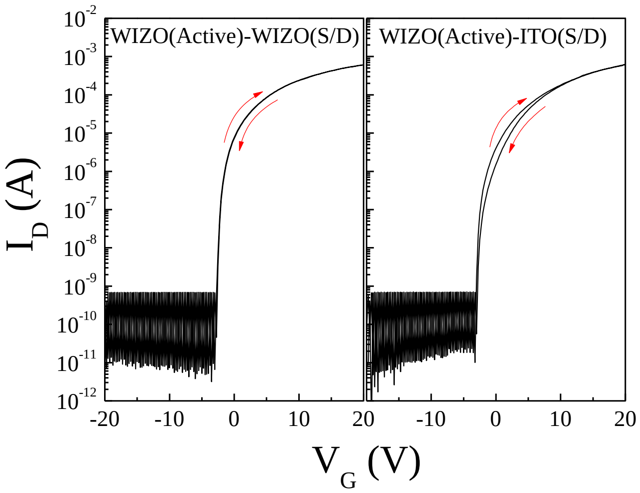


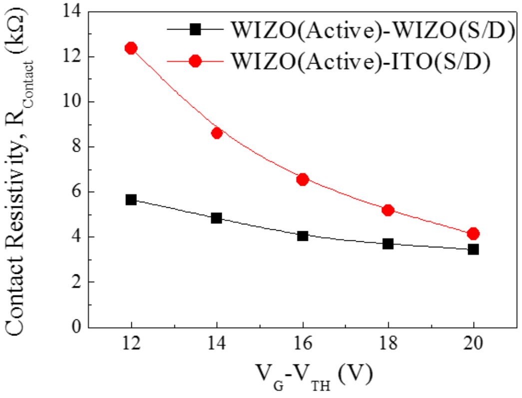


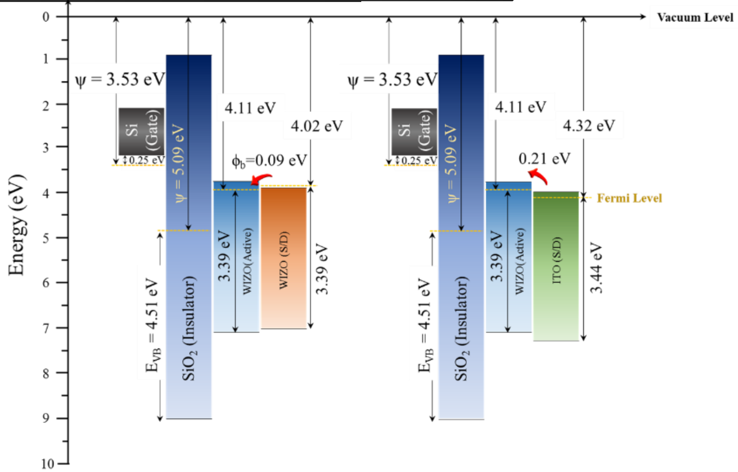
Target thickness (nm)	Physical properties			
	Real thickness (nm)	Film density (g/cm^3)	Interface roughness (nm)	Surface roughness (nm)
10	10.59	6.11	0.32	0.72
20	21.99	5.95	0.49	0.82
50	54.06	5.91	0.51	1.23
80	85.06	5.88	0.53	1.39
100	104.96	5.87	0.56	1.60

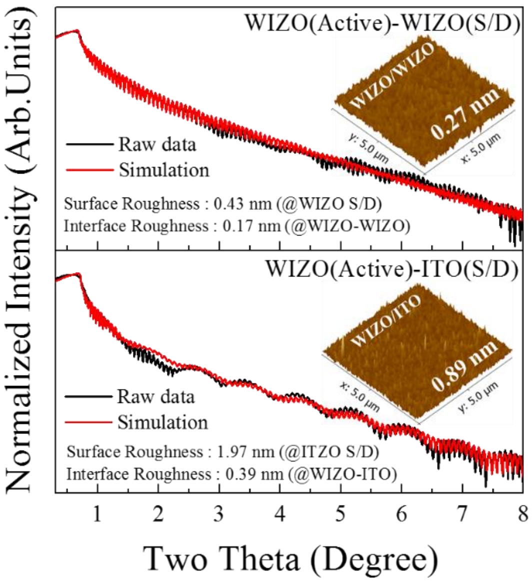
➔Relation between device performance and film density, interface roughness, interface trap density

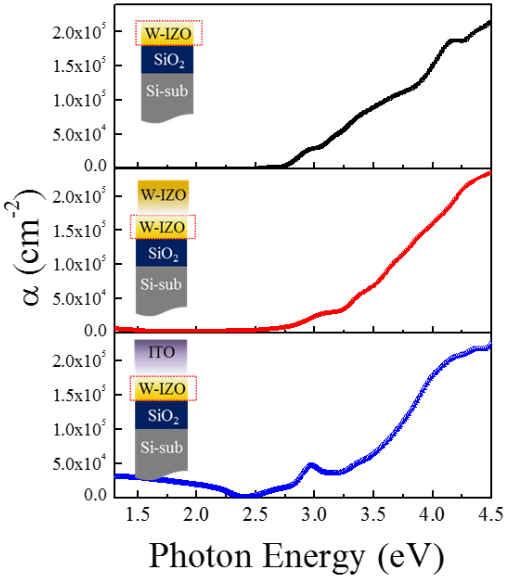
WInZnO TFT (Homojunction structure)

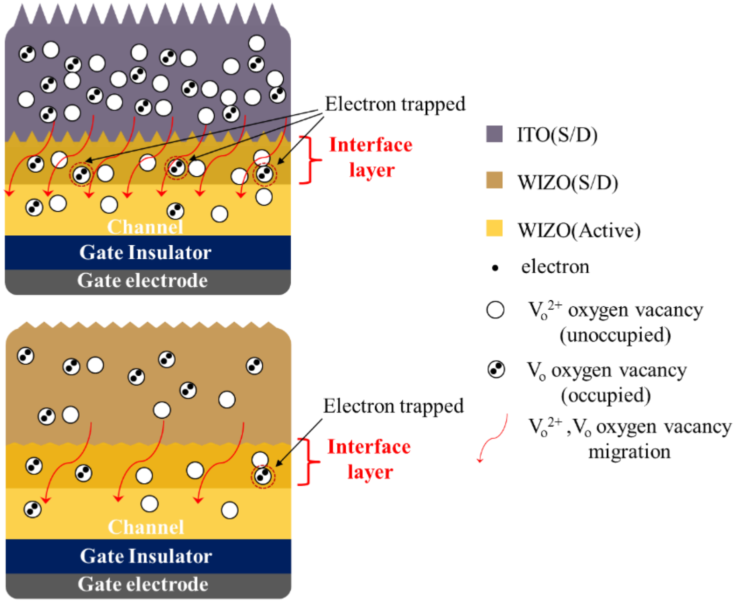






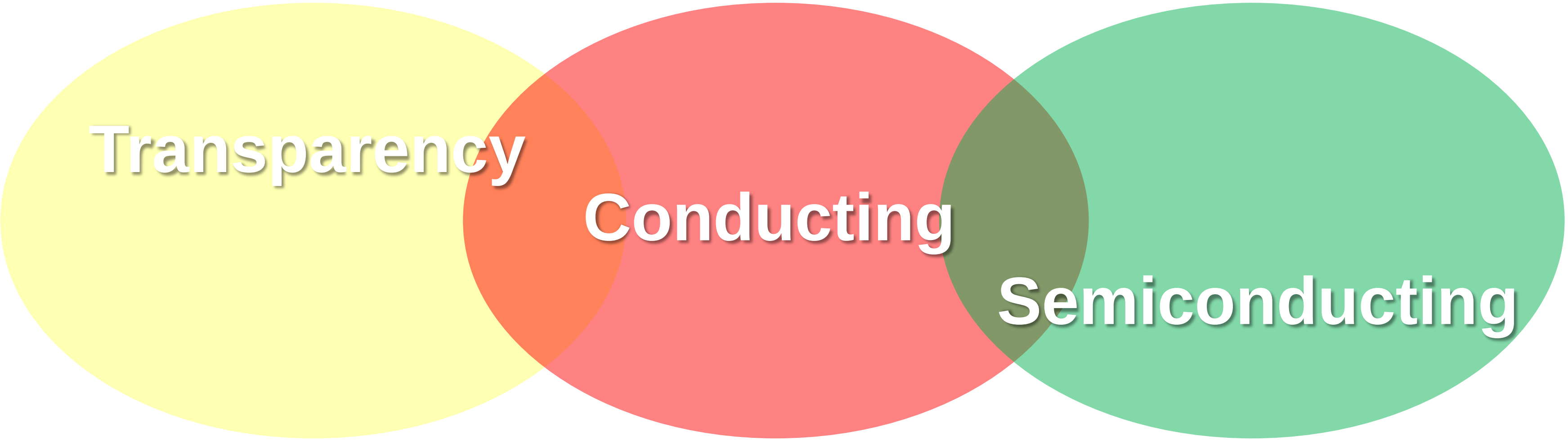






➔Homojunction structure is a method that can improve the device performance and Stability

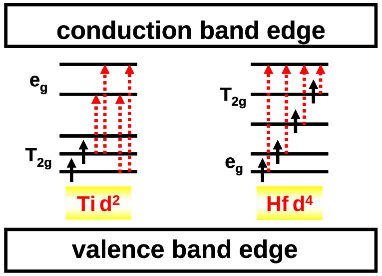
Summary



Transparency

Conducting

Semiconducting



Analysis of Electronic Structure

➔ *Conduction band, Band edge states, Band alignment, Binding states, Molecular orbital ordering*

Thank you for your attention!!