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Department of Engineering

Vacuum Deposited Ionic Oxide Semiconductors for Thin Film Transistors and Solar Cells

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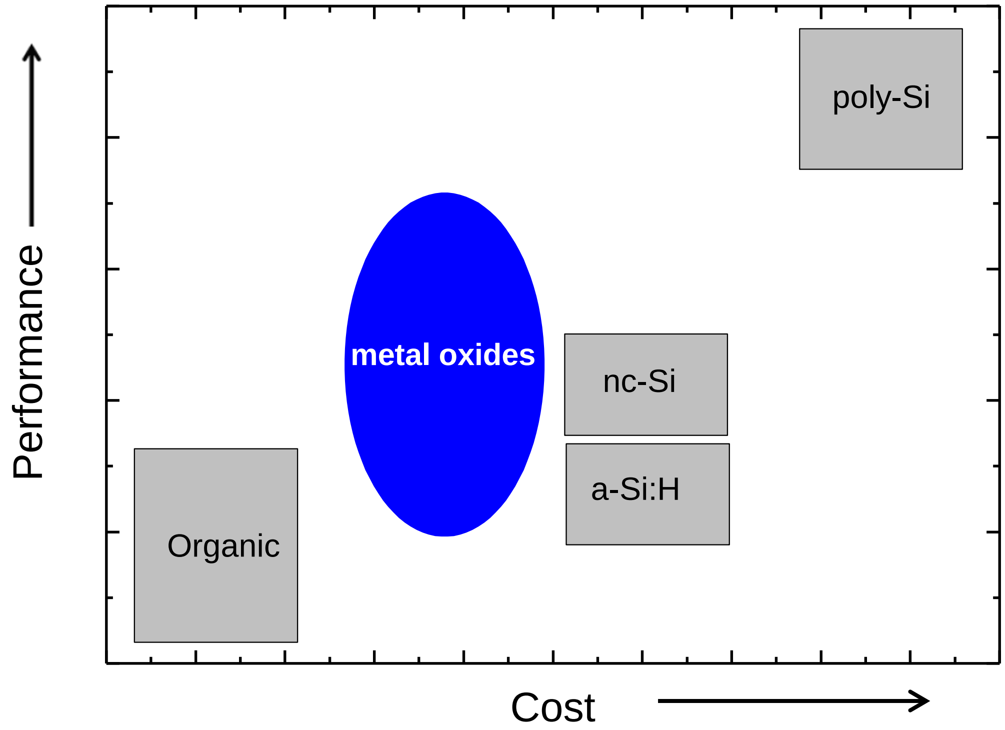
ELECTRONIC DEVICES & MATERIALS GROUP

Outline

- Introduction
  - Materials for large area electronics
  - Deposition technology comparison
- HiTUS sputtering
  - Zinc Tin Oxide
  - Nitride/Oxynitrides
  - Hafnium Oxide
- PECVD
  - Zinc Oxide
- Conclusions

Materials for Large-Area Electronics



Deposition Technologies for Metal Oxides

- Sol-gel (non-Vacuum)
  - ✓ Low cost
  - × High temperature annealing
  - × Small substrates/scaling issue
  - Roll-to-Roll manufacture in development stage

- ALD/PLD (Vacuum)
  - ✓ Excellent quality films
  - ✓ Coating patterns with high aspect ratio
  - × Slow deposition rate (<1 nm min^{-1})
  - Scaling issue

- Sputtering (Vacuum)
  - ✓ Good quality, highly uniform film
  - ✓ Room temperature depositions
  - ✓ Mature technology
  - ✓ Scalable for large area production
  - × Film stress/ ion induced damage

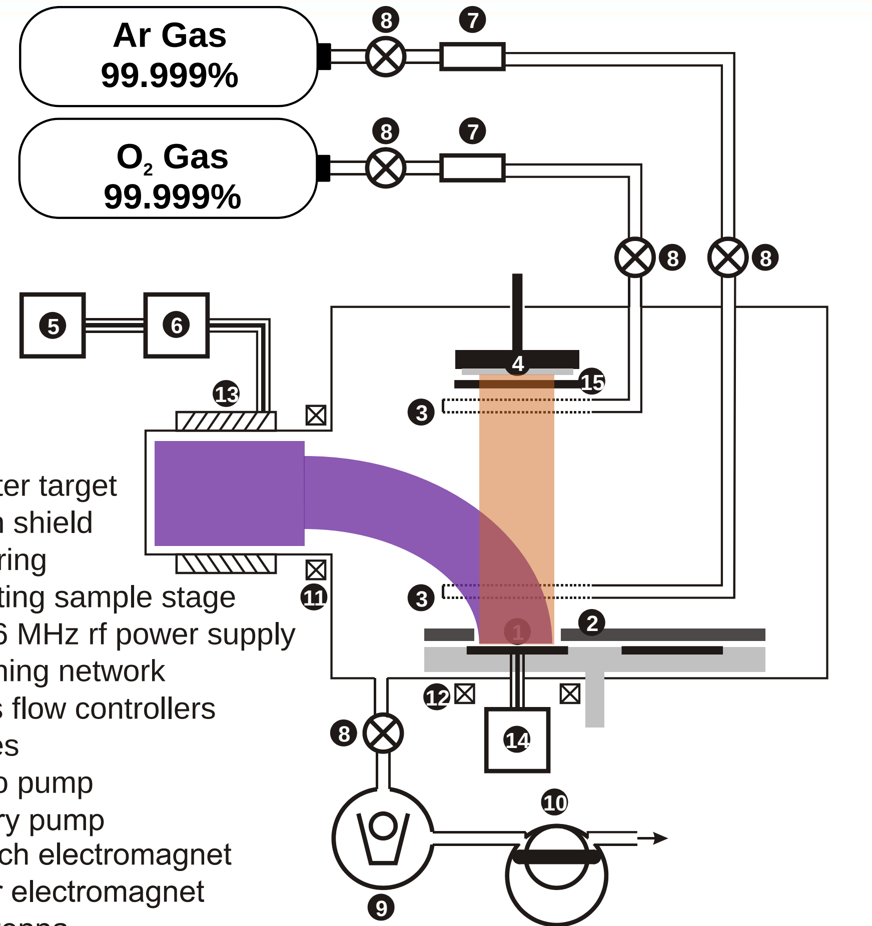
- PECVD (Vacuum)
  - ✓ Highly uniform film over large area
  - ✓ Deposition temp <300°C possible
  - ✓ Technology for a-Si:H production
  - ✓ Deploy older Gen tools for oxides?
  - × Handling of chemicals

High Target Utilisation Sputtering (HiTUS)

HiTUS Sputtering System

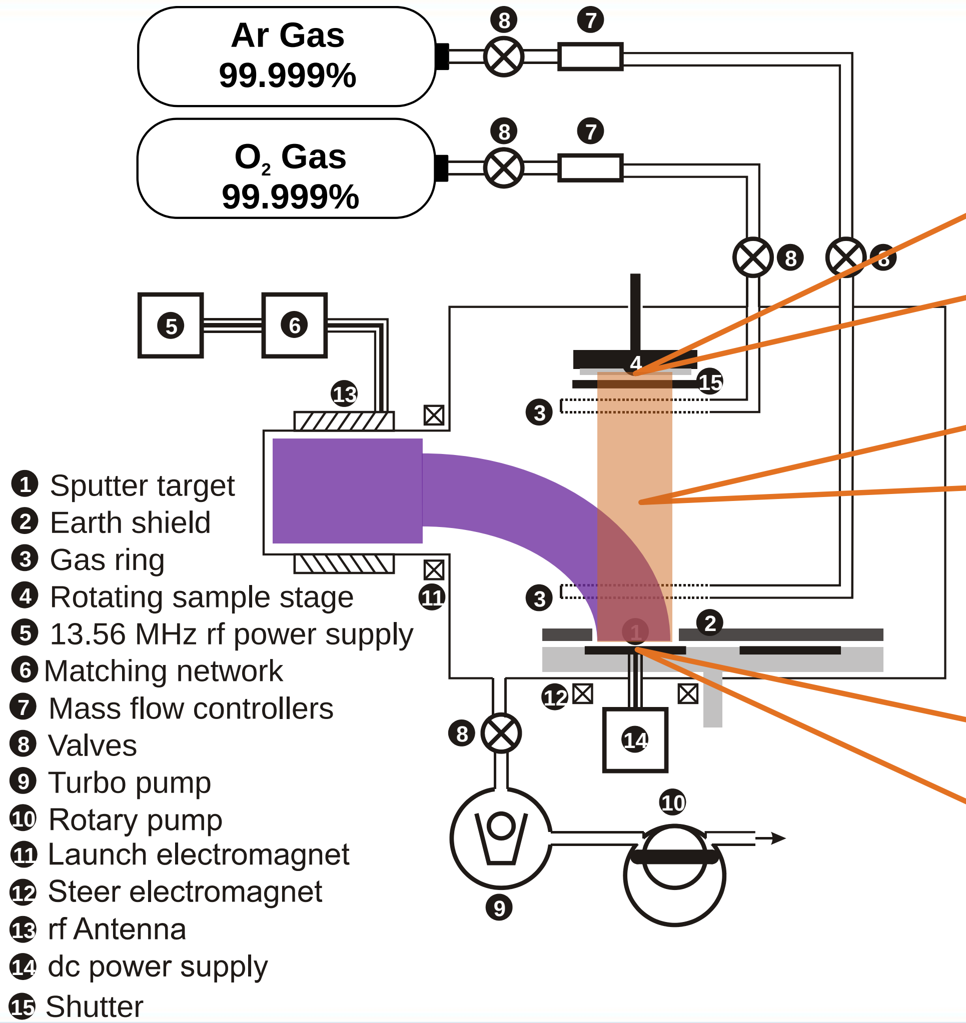
PQL

- ✓ Independent control of plasma density and sputtering ion energy
  - ✓ Excellent control of material properties including stress
- ✓ Sample removed from sputtering plasma
  - ✓ Reduced sample ion bombardment
- ✓ High target utilisation
  - ✓ High deposition rate



1. Sputter target
2. Earth shield
3. Gas ring
4. Rotating sample stage
5. 13.56 MHz rf power supply
6. Matching network
7. Mass flow controllers
8. Valves
9. Turbo pump
10. Rotary pump
11. Launch electromagnet
12. Steer electromagnet
13. rf Antenna
14. dc power supply
15. Shutter

Sputtering Processes



- Deposition of metal species
- Deposition of metal oxide species
- Oxidation

- Gas phase oxidation and thermalisation due to collisions

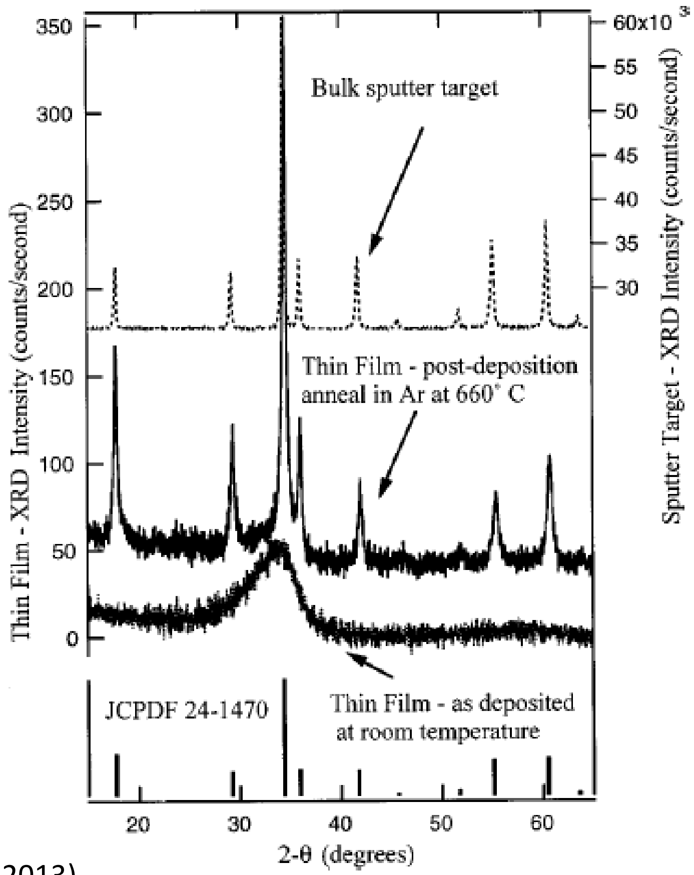
- Sputtering of substrate material by Ar^+ ions
- Oxidation of target surface (poisoning)

HiTUS Materials

n-type Zinc Tin Oxide

Background/Motivation

- Contact electrodes, TCOs
  - ✓ Optical BG > 3 eV
  - ✓ Polycrystalline : $ZnSnO_3$ and Zn_2SnO_4
  - ✗ $\rho \sim 4 \times 10^{-3}\ \Omega$ cm
- Channel layer in TFTs[1]
  - ✓ Amorphous but still high mobility
  - ✓ Indium free
- Used in solar cells, sensors, passivation[2-4]
  - ✓ high ρ, conformal film
  - ✓ chemical resistance



Young *et al.*, JAP **92**, 310 (2002)

[1] Chiang *et al.*, APL **86**, 013503 (2005) [2] Lee *et al.,* Energy & Environmental Science **6,** 2112 (2013)

[3] Dutta *et al.,* Sensors and Actuators B: Chemical 143, 50 (2009)

[4] Kim *et al.*, J. of Physics D: Applied Physics 47, 385104 (2014)

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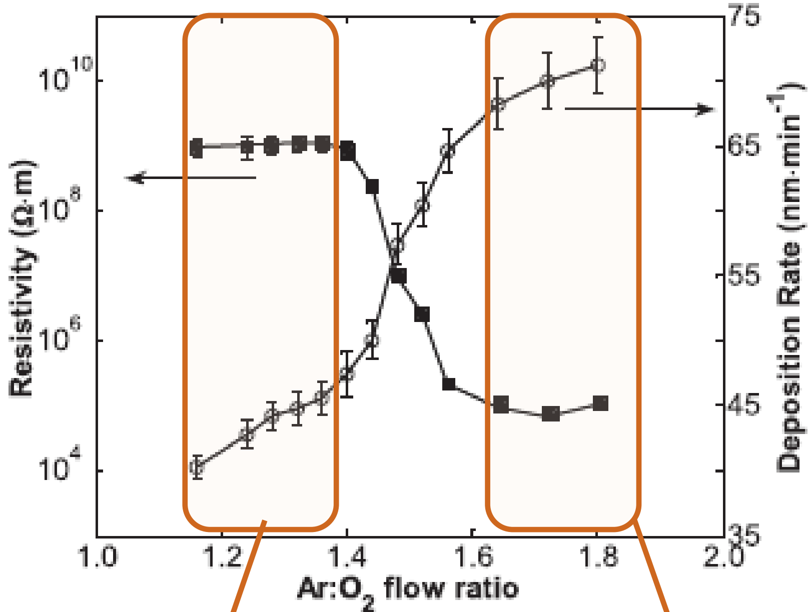
ZnSnO sputtering

- Sputtered from Zn:Sn alloy targets
- Zn:Sn atomic ratio in target
  - 50%:50% (i.e., $ZnSnO_3$)
  - 67%:33% (i.e., Zn_2SnO_4)
  - 90%:10%
  - 100%:0% (i.e., ZnO)
- Process parameters
  - $Ar:O_2$ gas flow ratio
  - Sn compositions
- Issues in alloy target
  - ✗ material depletion (e.g. InZnO)

HiTUS ZnO



- Oxygen rich
- resistive film
- low depo. rate

- Insufficient oxidation
- Metallic film

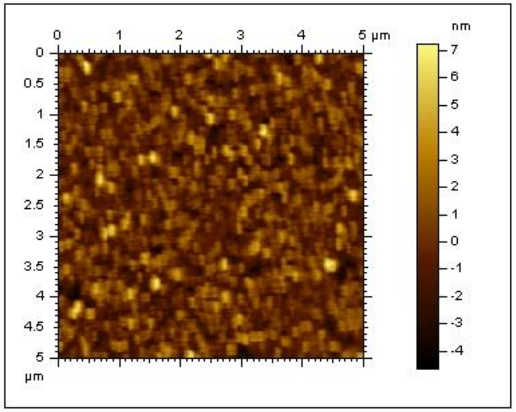
Garcia-Gancedo *et al.*, JAP **112**, 014907 (2012)

ZnSnO – growth rate and resistivity

- Lauch/target power : 800/500 W
- Growth rate and resistivity is tunable in ZnSnO as in ZnO
- All ZnSn compositions show similar correlation
- Conditions for TFTs identified
  - ρ_H range : 10^6 Ω-cm
  - Rate ~ 15 nm min^{-1}
  - Ar: O_2 flow ratio : 1.2 -2.2

ZnSnO results

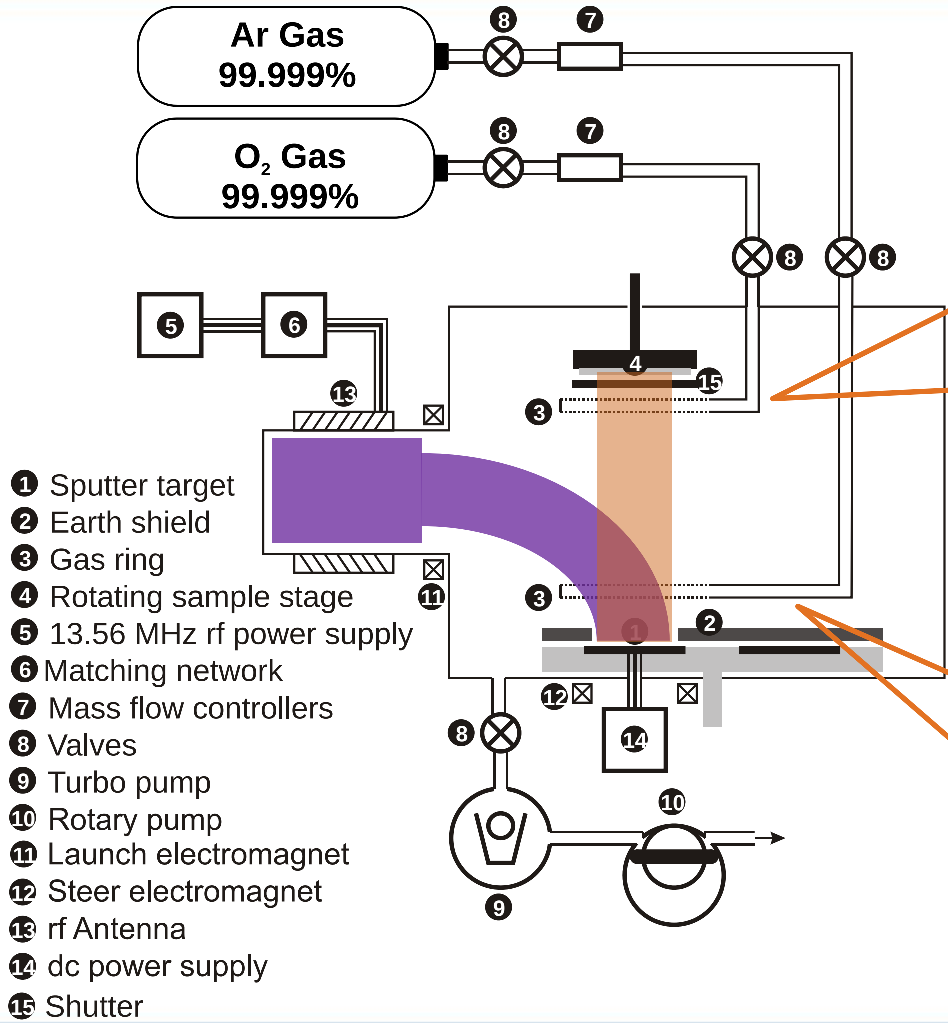
- Structural properties
  - XRD confirm films still amorphous after 500 ^{o}C anneal
  - Surface roughness r.m.s ~ 1 nm
- Optical properties
  - Transmission > 80 % in UV-Visible
  - Optical Tauc gap ~ 2.8 eV
- Transistors
  - enhancement mode
  - μ_{FE} 12- 20 cm^2 V^{-1}s^{-1}
  - Vth 8- 10 V
  - on-off > 10^8



HiTUS Materials

Nitrides/Oxynitrides

Sputtering Processes



N2 gas line near substrate

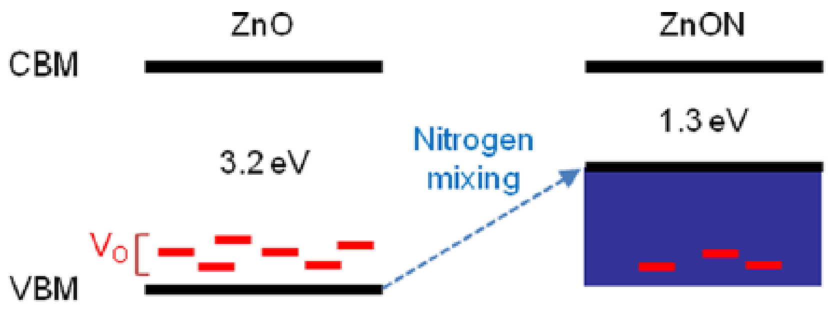
- Predominant Ar plasma
  - Oxides
  - N doped oxides
  - Nitrides (?) (w/o oxygen)

N2 gas line near target

- Predominant N_2 plasma
  - N doped oxides/Oxynitrides
  - Nitrides (w/o oxygen)

Background/Motivation

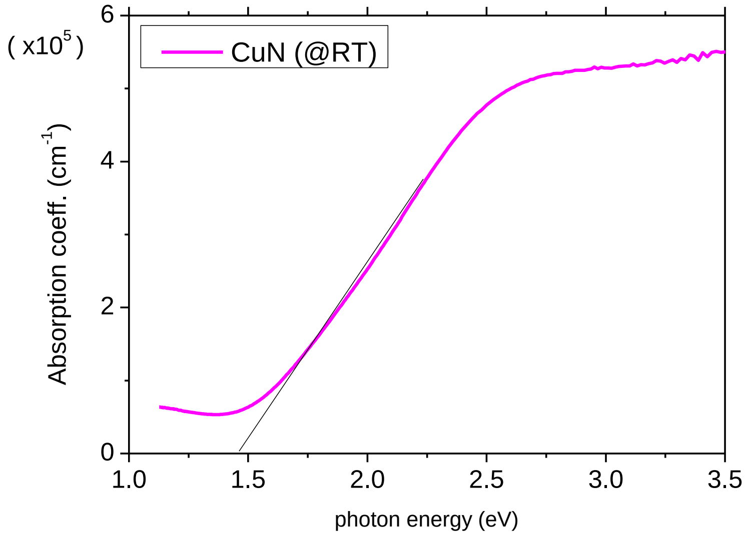
- Simple, binary oxide/nitride system (vs. IGZO, GZTO, ZTO, ITO)
- Anion doping/control (vs. cation control)
- Copper Nitride
  - (potential) p-type semiconductor
  - p-type semiconductors needed for CMOS, p-n junction diode
  - earth abundant semiconductor
  - Development for Solar cells
- Zinc Oxynitride
  - n-type semiconductor
  - Simple binary oxide for TFTs
  - Lower photosensitivity

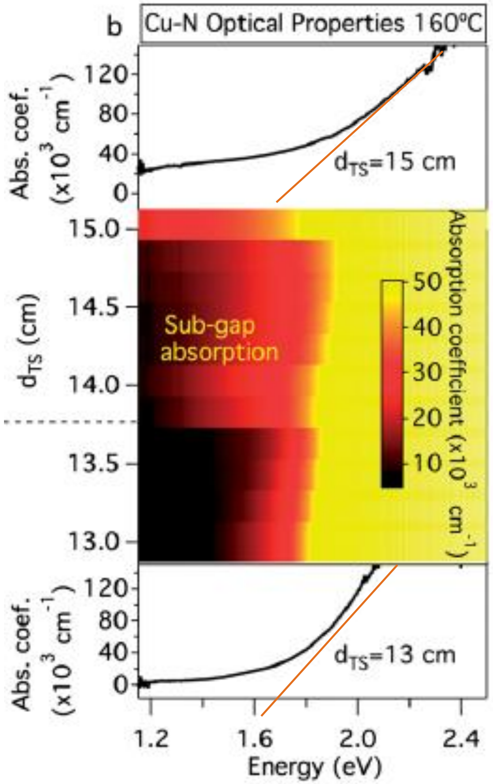


Ryu M. et al., IEDM 2012, 5.6.1 - 5.6.3

Copper Nitride –Optical properties

- Transmission max. 60% at 850 nm
- Absorption edge ~ 1.5 eV, close to value reported in literature





Caskey *et al.*,Mater. Horiz. (2014) **1**, 424

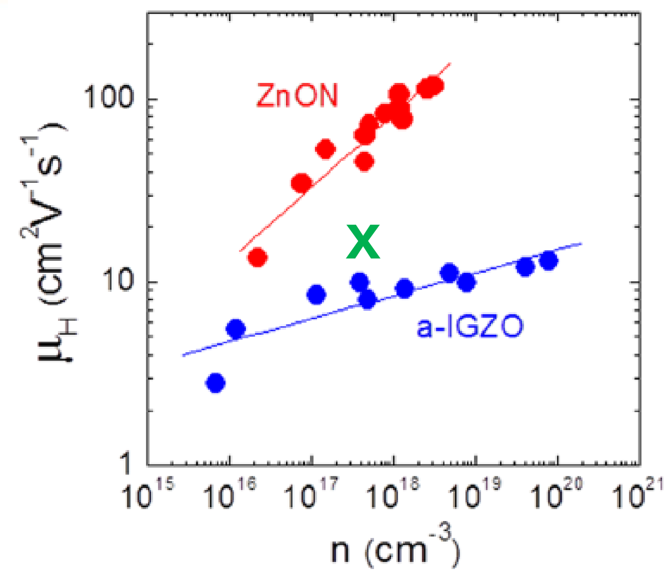
Copper Nitride – Electrical & structural properties

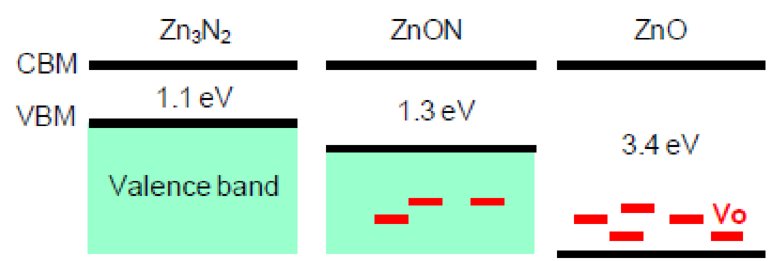
- Structural
  - preferential orientation (00L) which occurs at higher N_2:Ar ratio[1]
  - But, small grain (~20 nm)
- Electrical
  - Carrier density ~ 10^{19} cm^{-3}
  - ρ_H ~ 1 -6 Ω-cm
  - Mobility ~ 0.1 cm^2 V^{-1} s^{-1}
  - Hole/electron (majority holes)

[1]Yue et al., J. Crystal Growth **274**, 464 (2005)

Zinc Oxynitride/nitride

- Carrier type : electron (n-type)
- Growth rate 15-17 nm min^{-1}
- Zinc Oxynitride
  - Mobility ~ 12 cm^2 V^{-1} s^{-1}
  - ρ_H ~ 1 Ω-cm
  - Carrier density ~ 4 x 10^{17} cm^{-3}
  - Optical BG ~1.5eV
- Zinc Nitride
  - Mobility ~ 35 cm^2 V^{-1} s^{-1}
    (vs.~ 100 cm^2 V^{-1} s^{-1} in ref. 2)
  - ρ_H ~ 4 Ω-cm
  - Carrier density ~ 5 x 10^{16} cm^{-3}
  - Optical BG ~ 1.1eV





[1] Ryu M. et al., IEDM 2012, 5.6.1 - 5.6.3

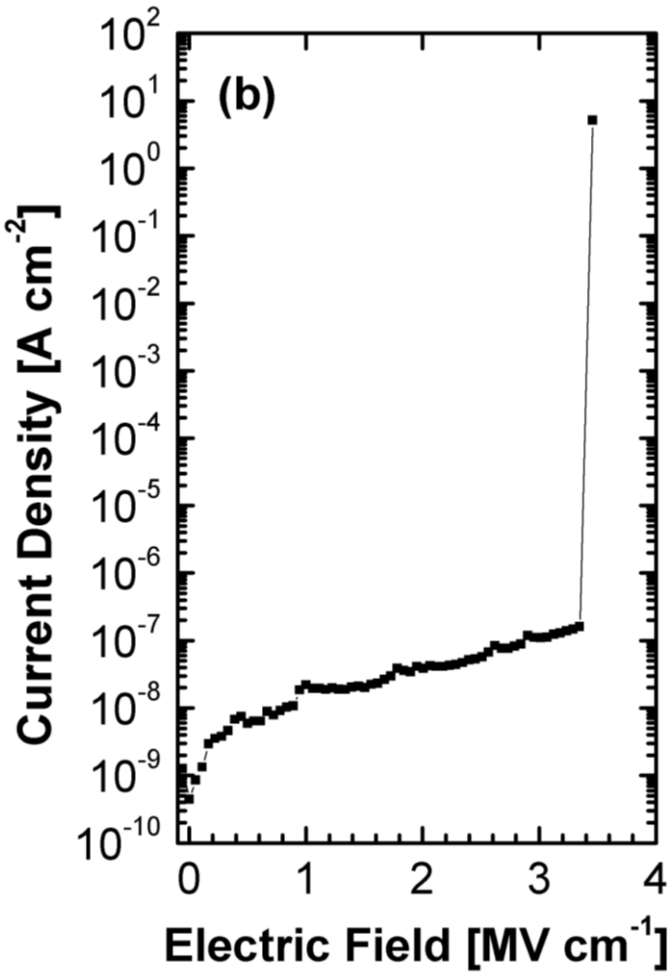
[2] Futsuhara et al., Thin Solid Films 520, 1278 (1998)

HiTUS Materials

Hafnium oxide

Hafnium Oxide

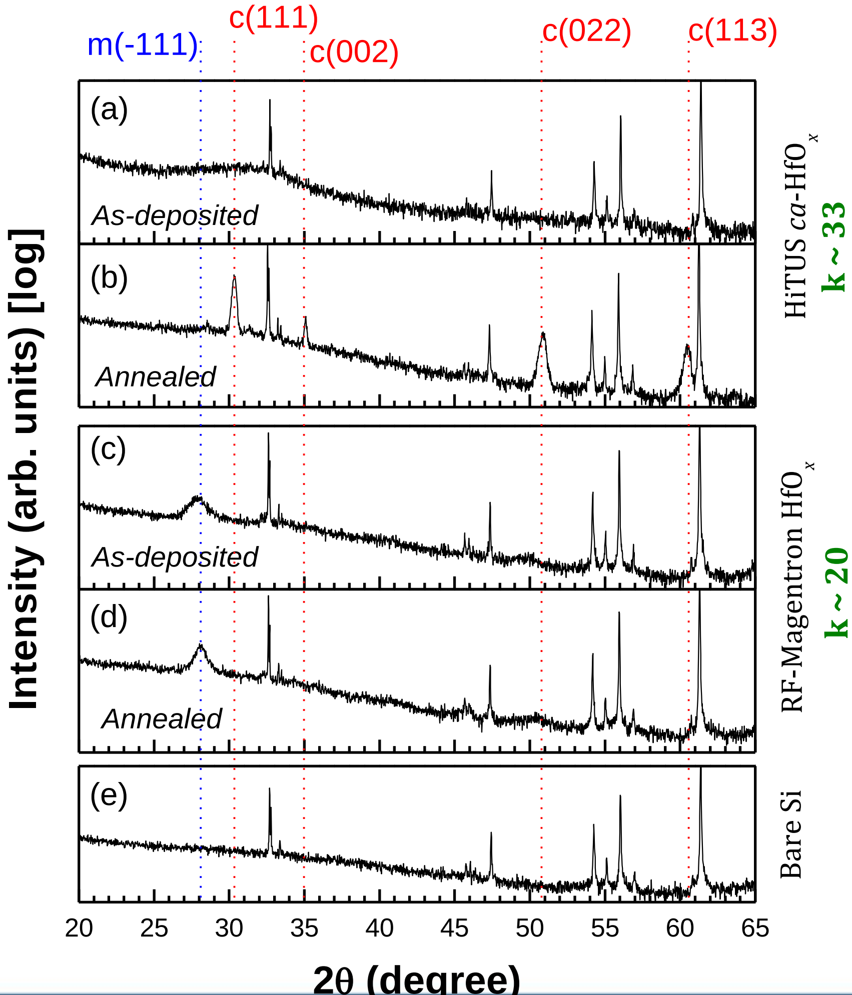
- Resistivity ~ $1.4 \times 10^{14}\ \Omega$ cm
- Breakdown ~ 3 MV cm^{-1}
- Dep. Rate ~ 25 nm min^{-1}
- >90% optical transparency in visible
- Amorphous film
- Dielectric constant ~ 33



Li *et al.*, Phys. Status Solidi B **250**, No. 5 (2013)

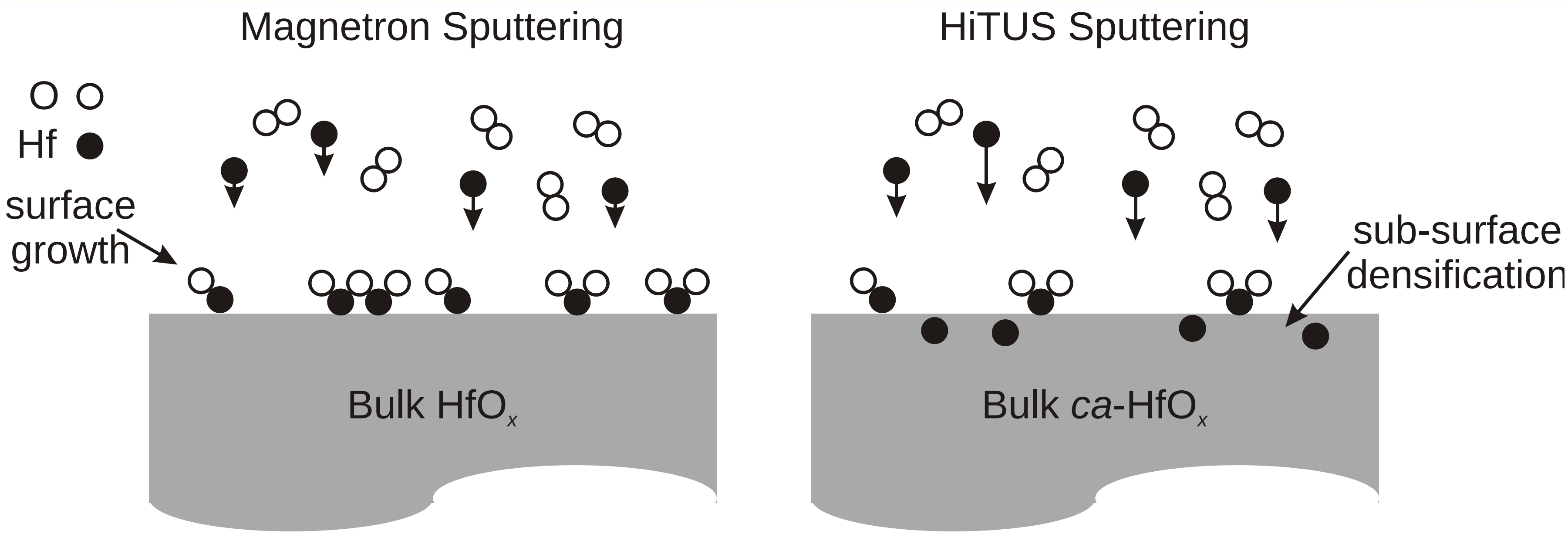
Hafnium Oxide

- Annealing at 640°C in vacuum
- Cubic-like amorphous hafnium oxide (*ca*-HfO_x)
  - ✓ HiTUS film (k ~33)
  - × Rf magnetron (k~20)



Li *et al.*, Phys. Status Solidi B **250**, No. 5 (2013)

Cubic-like Amorphous Hafnium Oxide (*ca*-HfO_x)



- Magnetron sputtering: Hf energies up to ~35 eV
- HiTUS sputtering: Hf energies up to ~125 eV

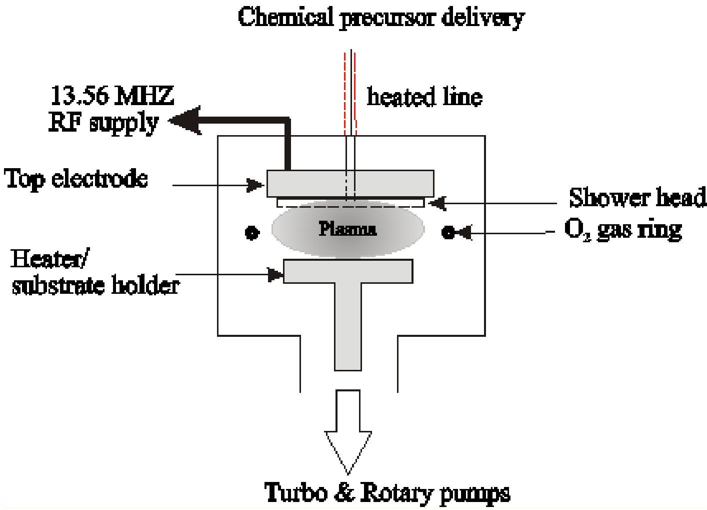
→**HiTUS process allows Hf subplantation leading to film densification and *ca*-HfO_x phase**

Li *et al.*, Phys. Status Solidi B **250**, No. 5 (2013)

Plasma Enhanced Chemical Vapour Deposition (PECVD)

PECVD for development of metal Oxides

- Home built PECVD system
- Capacitive discharge between parallel electrodes
- Plasma by RF @13.56 MHz
- Dep. Temperatures < 300ºC possible with plasma assistance
- Easy tuning of material composition and phase
- Scalable for large area



Challenges

- Difficulty in handling organometallic precursors
  - Many are pyrophoric
  - sensitive to air and moisture
  - Usually low vapour pressures
  - need to be volatile and reactive at process temperatures, but stable enough to prevent premature decomposition
  - sensitive to changes in temperatures and pressures
  - Need heated lines downstream of bubblers
- Precursor delivery systems
  - Vapour delivery (Classical bubbler system)
  - Direct Liquid Injection (DLI) system
  - Flash Vaporization

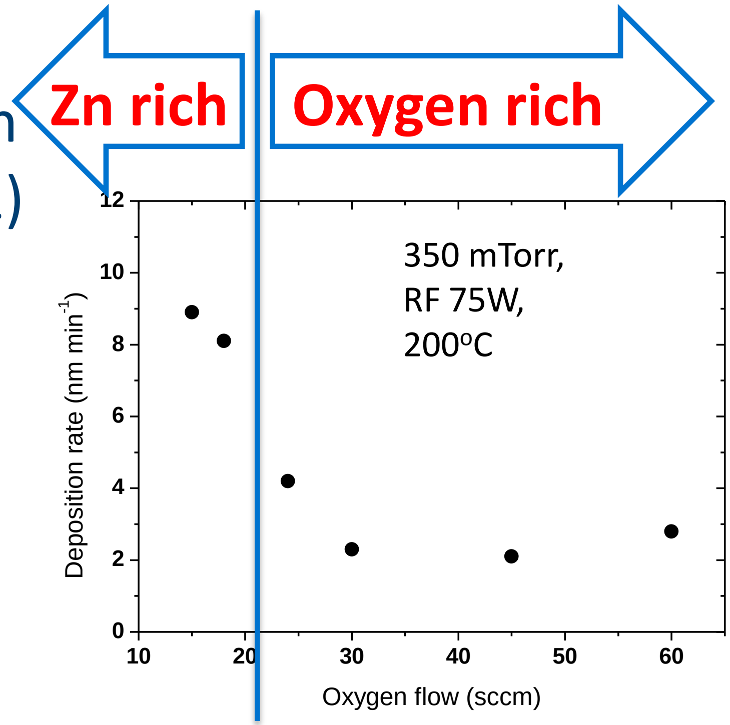
PECVD Materials

Zinc oxide

Zinc Oxide

- Precursors : Diethyl Zinc + Oxygen

- sub-stoichiometric
- Random orientation (002), (100) and (101)
- larger grain size ~ 30nm
- textured surface
- preferable for solar cells



- Stoichiometric
- Preferential orientation, (002) only
- smaller grain size (10- 20 nm)
- uniform surface
- preferable for TFTs

Conclusions

- Presented vacuum deposited oxide materials that has been developed/ currently developed at Cambridge
- HiTUS sputtering
  - High quality ZTO TFTs with potential lower processing temp.
  - Copper Nitride promising p-type material for solar cell
  - Zinc Oxynitride simple binary oxide with anion doping suitable for TFTs
  - High k (k=33) ca-HfO_x resulting from finer control of thin film microsctructure by HiTUS
- PECVD
  - Zinc Oxide with textured surface for solar cell

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