# Stability Issues of Transparent Conducting Oxides (TCOs) for Thin-Film Photovoltaics

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy operated by the Alliance for Sustainable Energy, LLC

# Outline

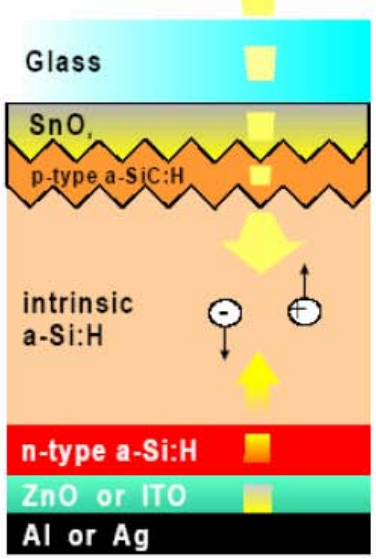
- **Background**
  - application of TCOs in all thin-film PV
- **Stability Issues**
  - -- Accelerated Tests and Results
    - -- ZnO, ITO, $SnO_2$ by Damp Heat (IEC 61646)
  - -- Impact on thin film PV encapsulation/construction
- **Solutions:**
  - New TCOs
  - Mitigation Methods
- **Conclusions**

# TCO in PV Applications

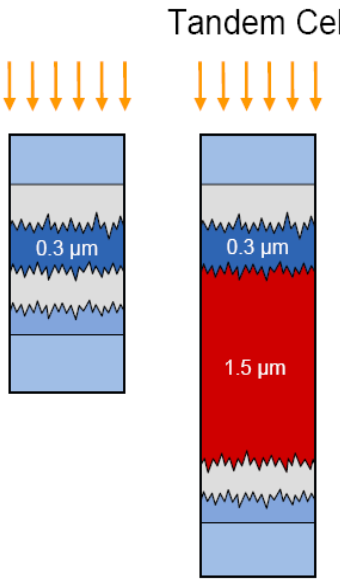
- Various TCOs are used in various thin-film PV technologies, ranging from a-Si to CIGS, CdTe, dye-sensitized, organic, and quantum-dot solar cells.

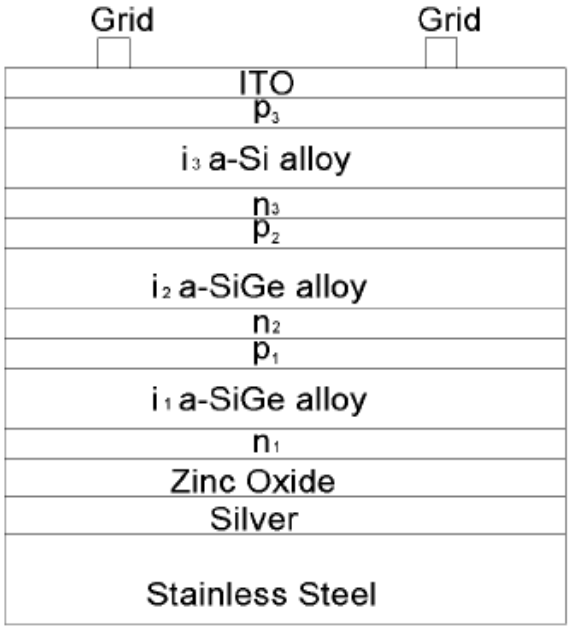
- Performance, Cost, and Thin-Film PV Fabrication Sequence (Substrate- or superstrate-type) are important factors in the selected use of TCO.

# Example-1: ZnO, ITO, and $SnO_2$ in a-Si & a-Si/µc-Si micromorph PV

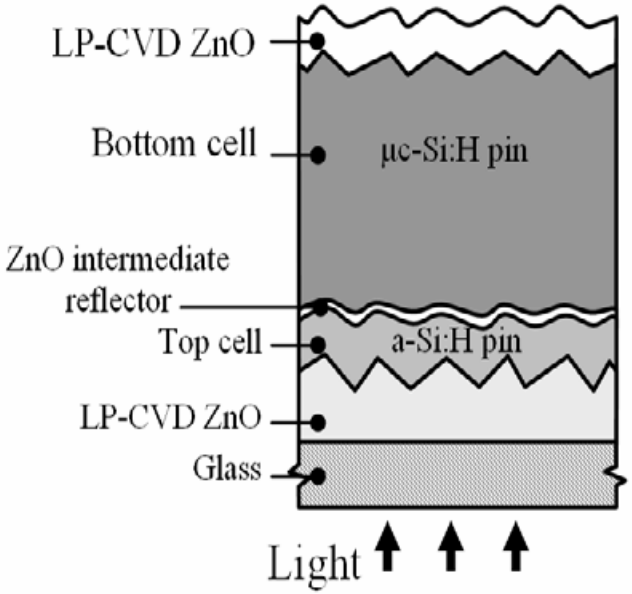



Single p-i-n junction a-Si Oerlikon Solar



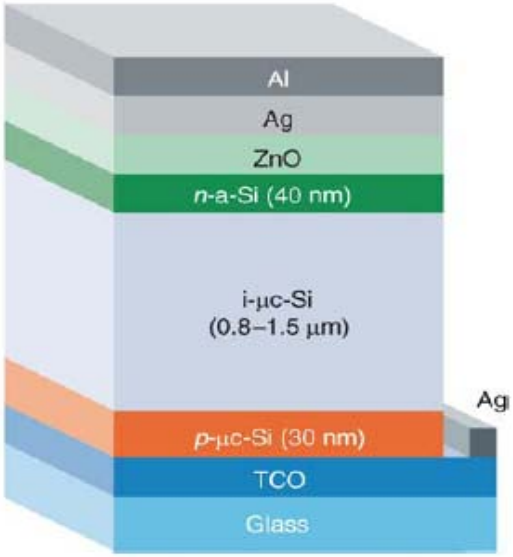




S. Guha, Uni-Solar Triple-Junction a-Si, MRS, 2004




D. Domine et al., IMT, 2005

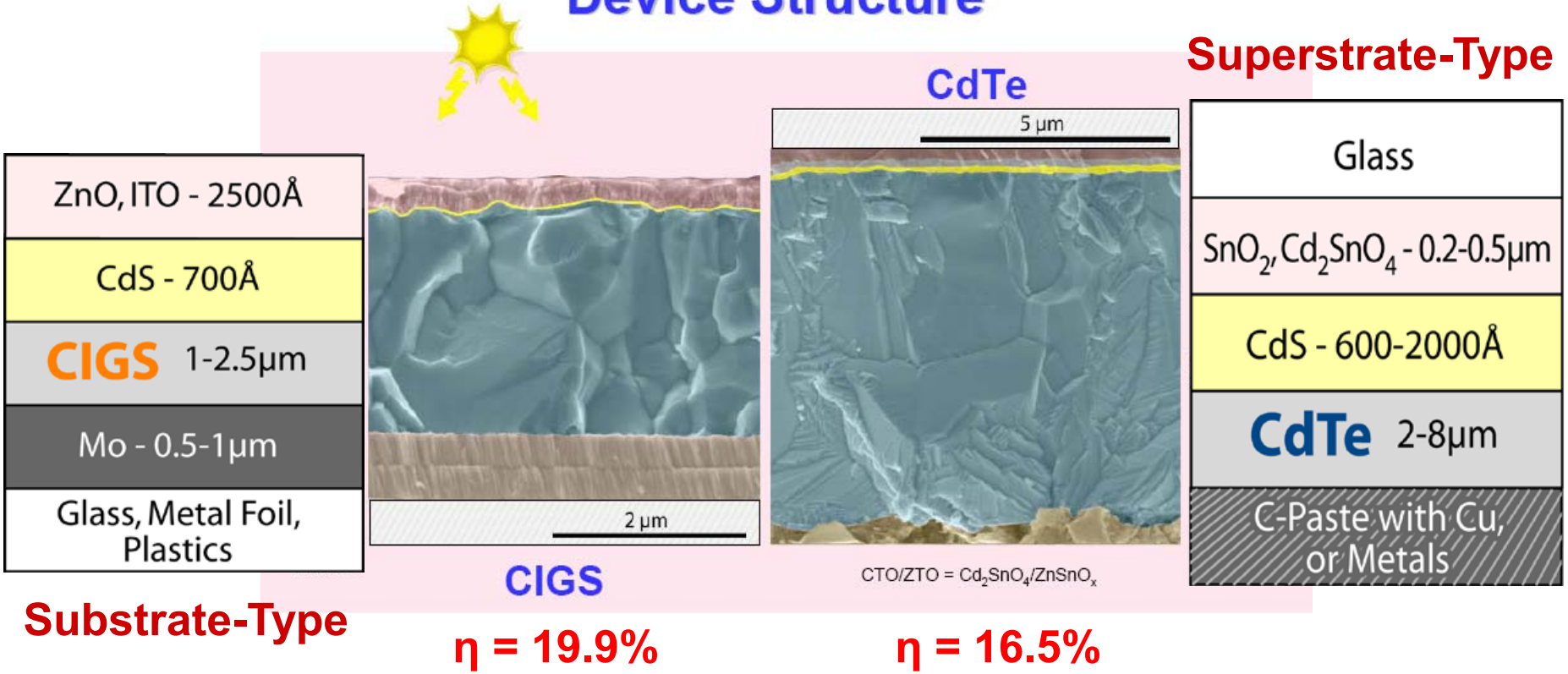
Sanyo Single junction p-i-n a-/µcSi



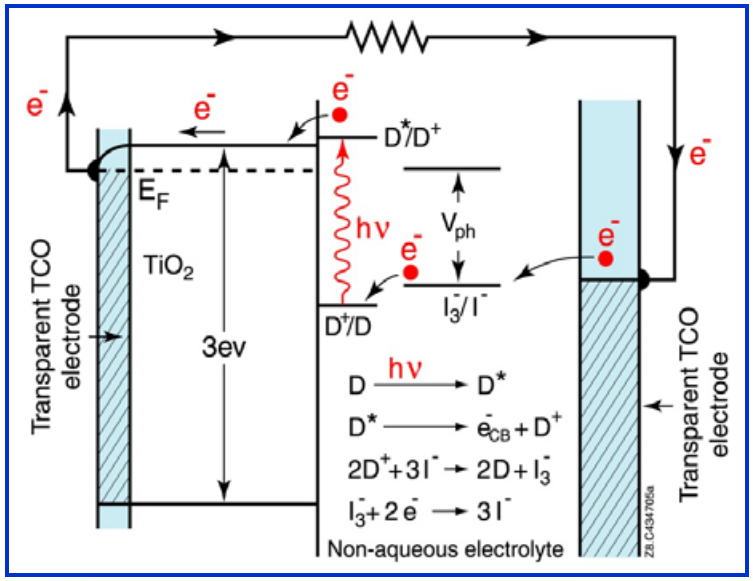

MRS BULLETIN • VOL. 32 • MARCH 2007

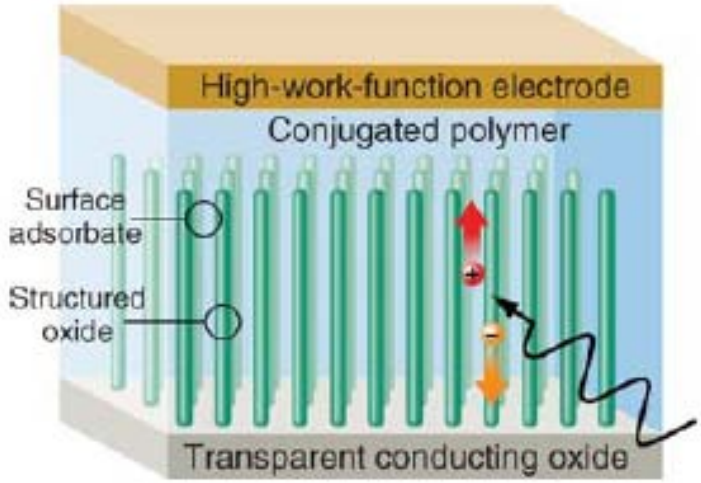
# Example-2: ZnO, ITO, $SnO_2$, $Cd_2SnO_4$ in CIGS and CdTe PV

## NREL's High Efficiency CIGS and CdTe Device Structure



# (Graetzel) Dye-Sensitized Solar Cell (DSSC)




**Nanowire DSSC**

# Example-3:

## Organic Solar Cell (OPV)

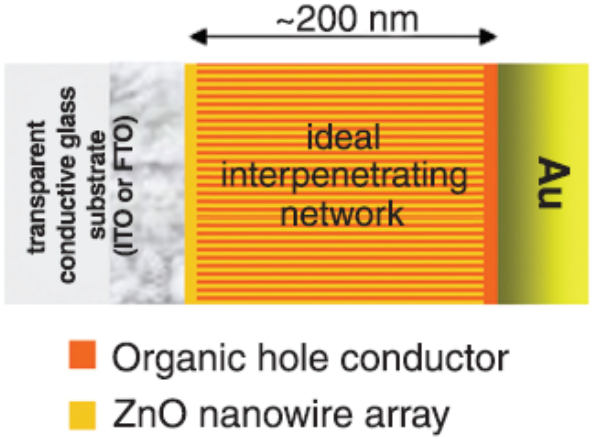
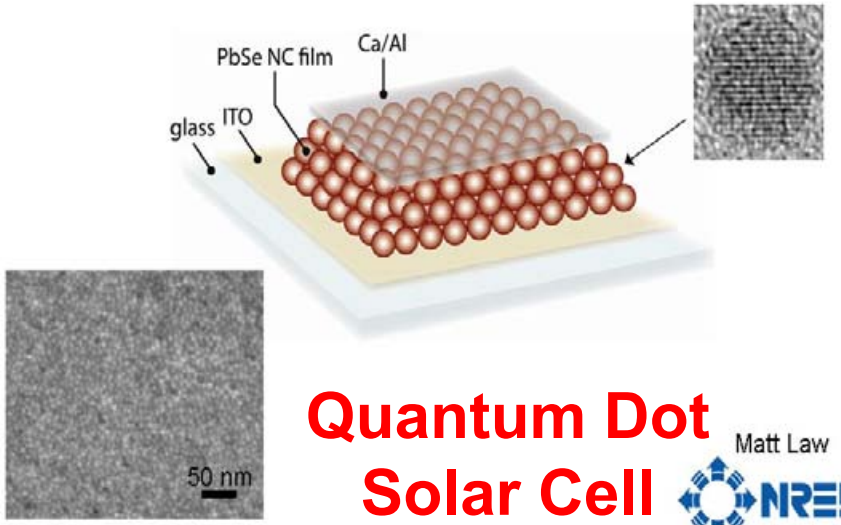



*Fig. 6 Schematic of a hybrid solar cell with an ideal interpenetrating network consisting of highly aligned and ordered ZnO nanowires and an organic hole transporter material.*




**Quantum Dot Solar Cell**

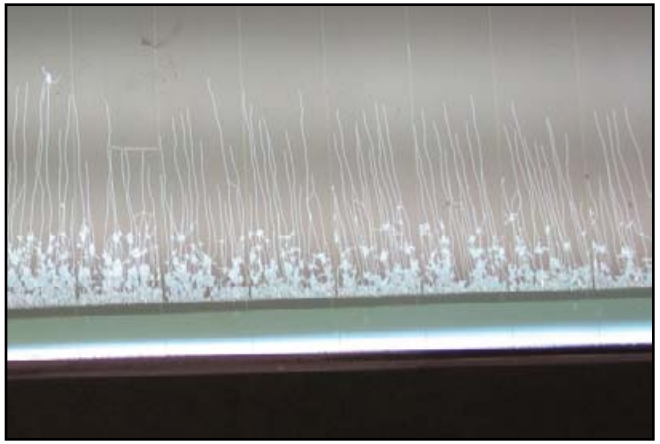
Matt Law

# Stability Issues of Thin Film PV

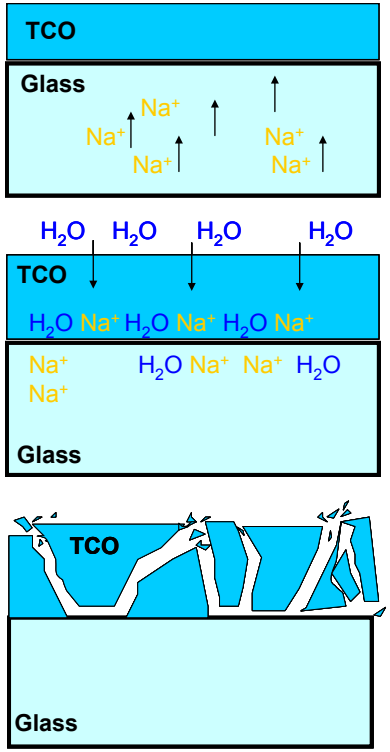
- **Two aspects: Absorber vs. TCO**
- **Absorber:** CIGS, CdTe, Organic (OPV)
  - sensitivity to moisture at elevated temperature.
- **TCO:** stability concerns as contact electrode or buffer layer or internal reflector
  - sensitivity to moisture and applied voltage at elevated temperature.

(This talk focuses only on TCO)

Corrosion



TCO Delamination




Negatively biased

# Material Stability of TCOs

## TCOs:

1. **ZnO for NREL CIGS:**
   - **single layer intrinsic ZnO (IZO)**
   - **single layer Al-doped ZnO (AZO)**
   - **Bilayer ZnO ( = i-ZO + AZO)**
   - **Al-doped $Zn_{1-x}Mg_xO$ alloys (ZMO, x = 1 – 10 %)**
2. **In-Sn-O (ITO,** commercial product)
3. **F-doped $SnO_2$** (commercial products and NREL)

## Accelerated Stress Exposures:

- **Mainly in Damp Heat (DH)--85°C/85%RH (IEC 61646)**
- **In DH with acetic acid vapor**
- **in a weatherometer (WOM) at 2.5 UV suns/60°C/60%RH**

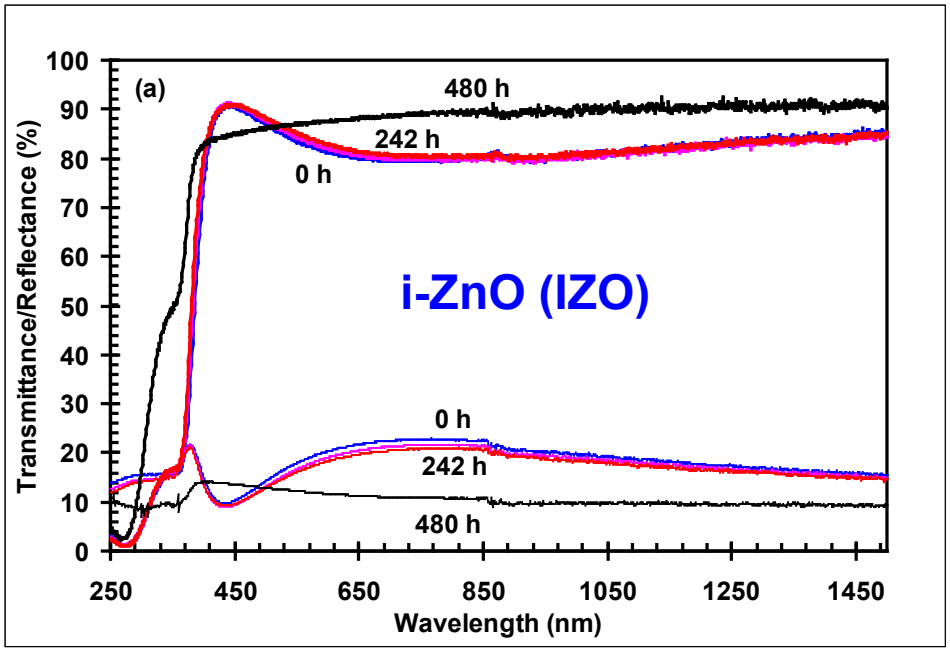
## Characterization:

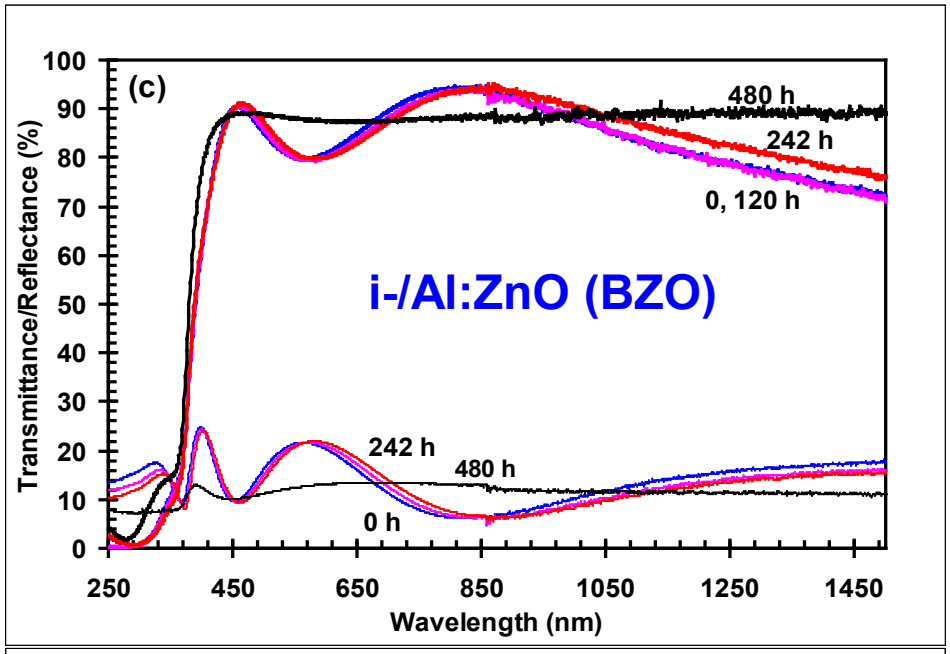
- **Optical** (T%, R%); **Electrical** (Hall, 4-probe);
- **Structural** (XRD); **Micro-imaging** (optical and SEM)

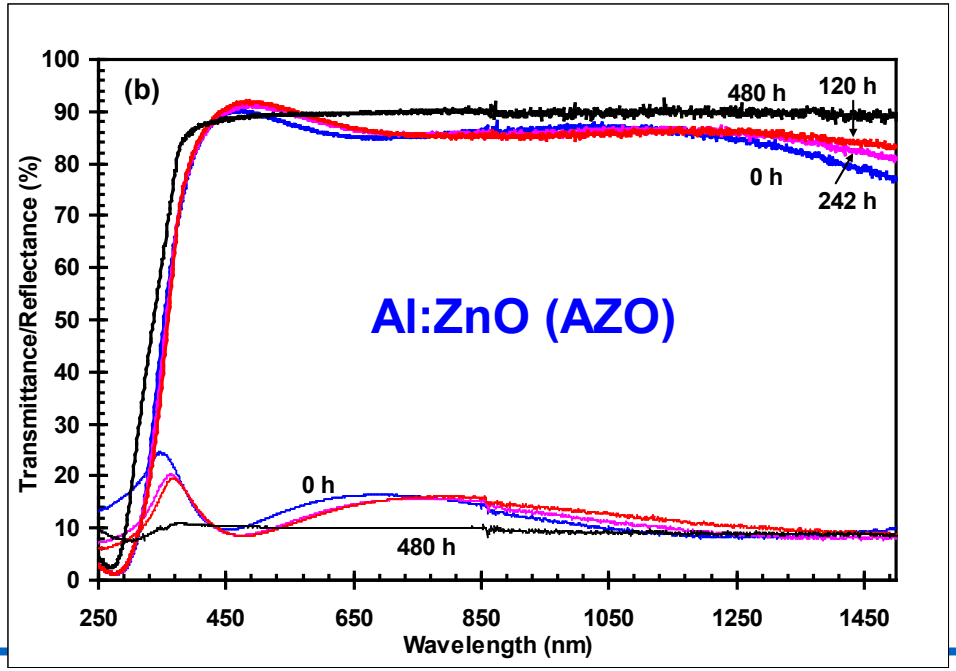
**Atlas Ci4000 WOM**

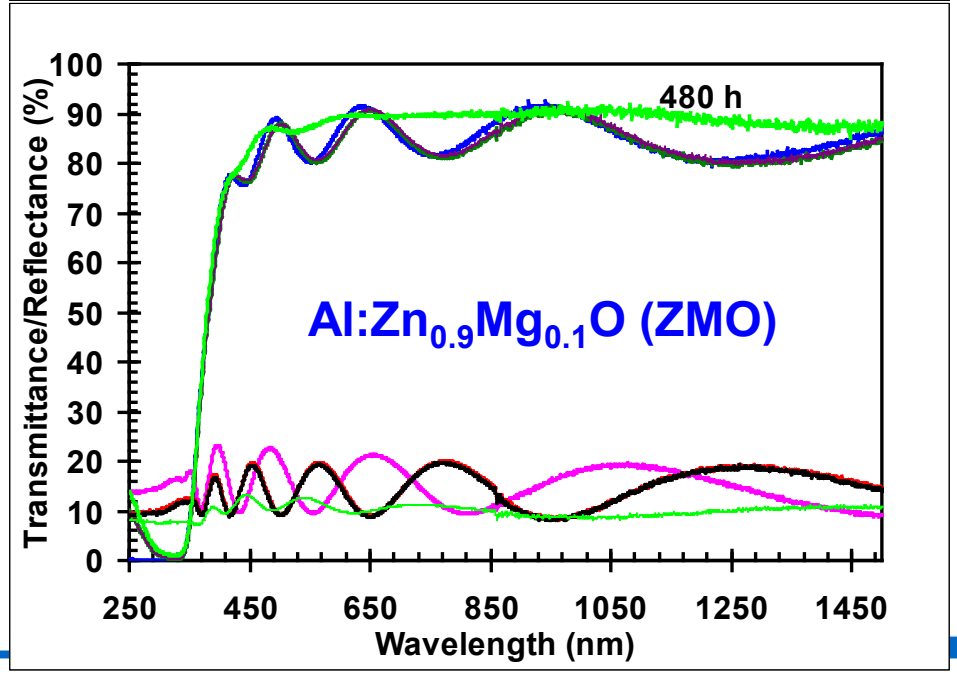
**=> To identify degradation mechanism and quantify degradation rates**

# Optical Degradation of ZnO & ZMO in DH

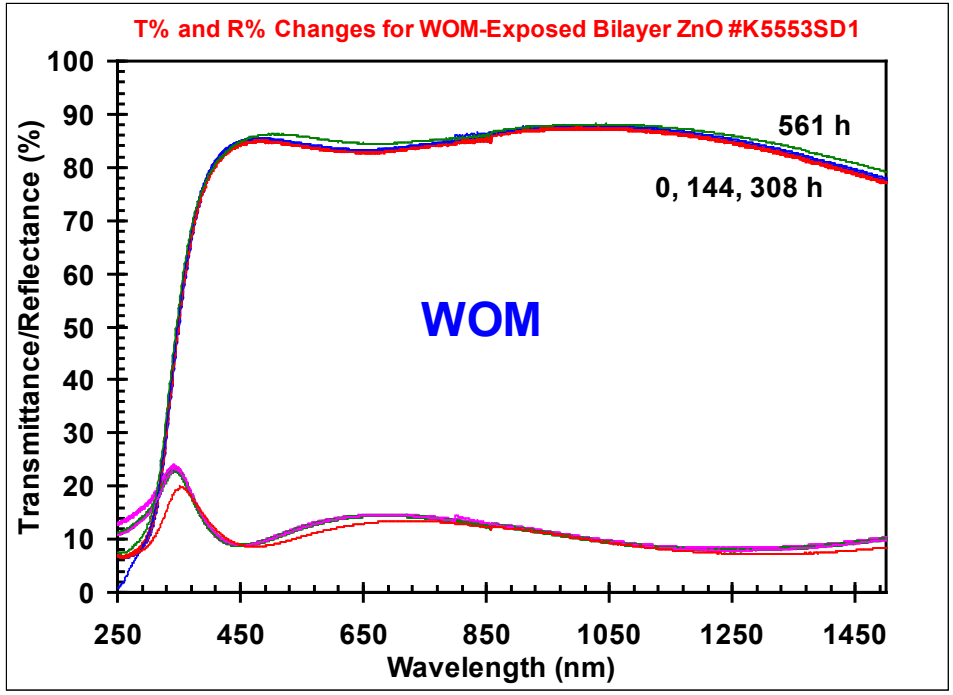


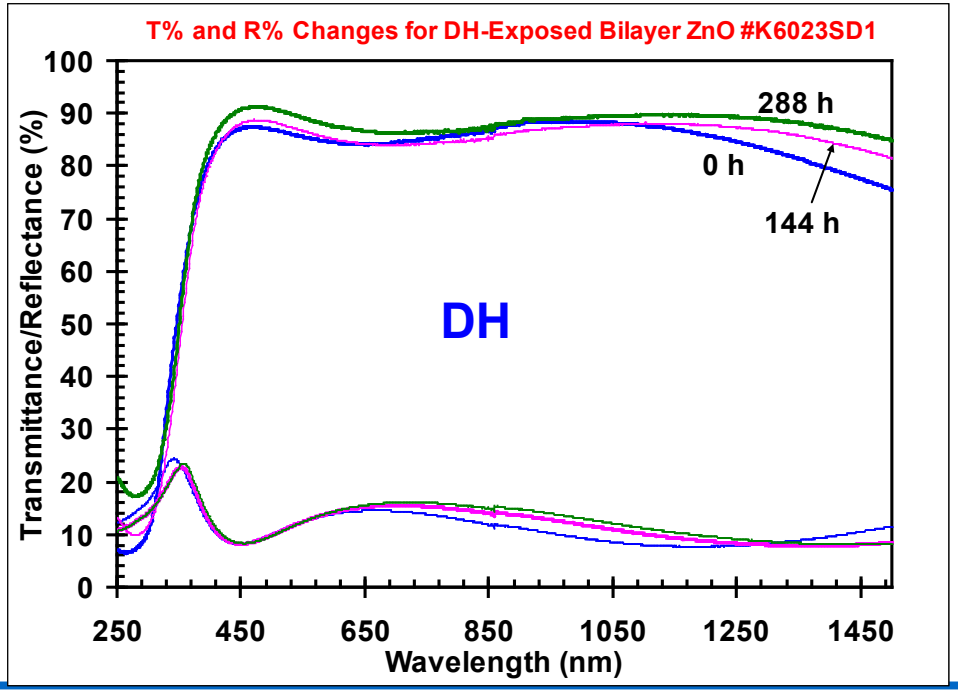



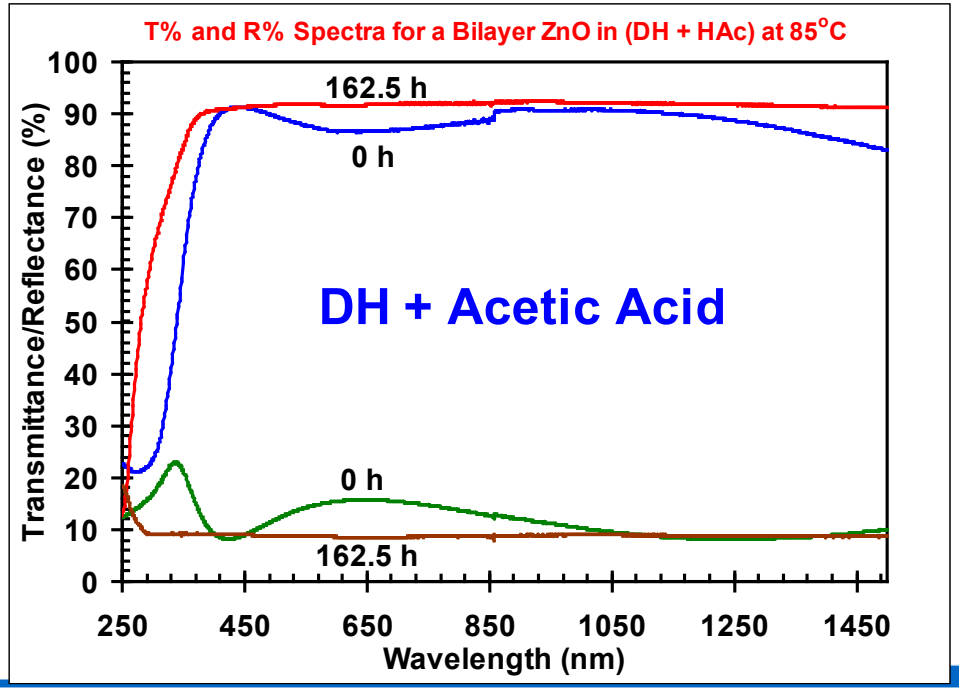
# Optical Degradation of Bi-layer i-/Al:ZnO (BZO)




## Degrading Effect:

- (DH + Acetic Acid) > DH > WOM
- Acetic acid rapidly destroyed ZnO and likely accelerated conversion into non-crystalline $Zn(OH)_2$

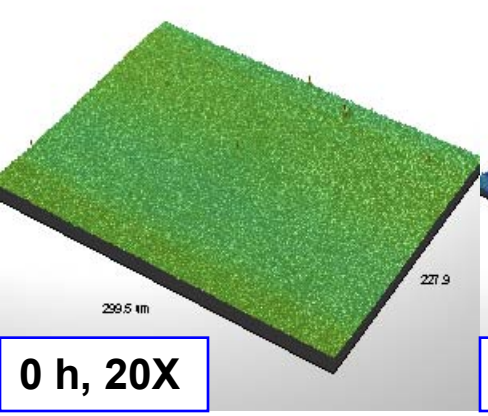


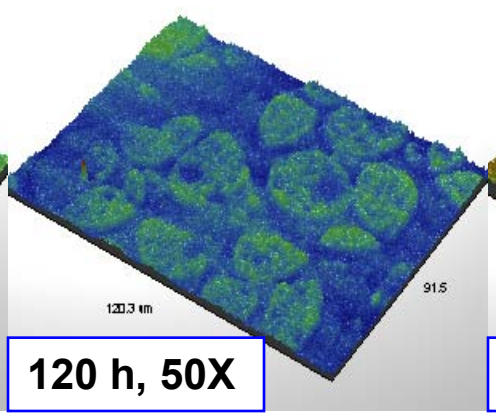
# Surface Morphology Changes on Al:ZnO & i-/Al:ZnO upon DH Exposures

## (WYKO Optical Interferometer)

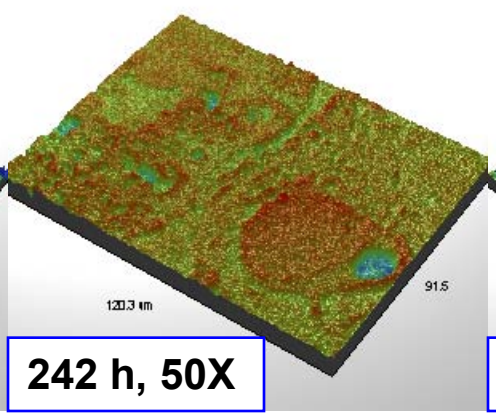
### Single-layer Al:ZnO (AZO), ~0.1 µm



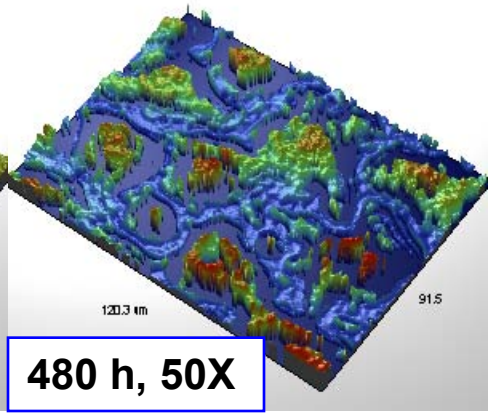

0 h, 20X




120 h, 50X

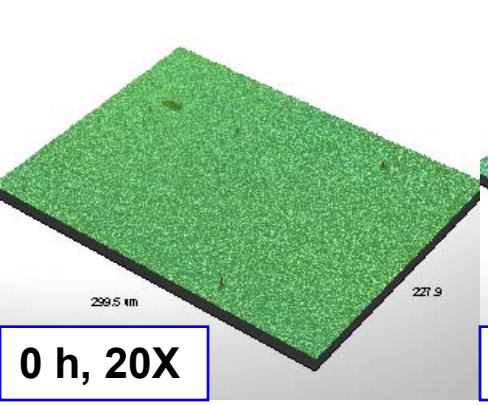



242 h, 50X

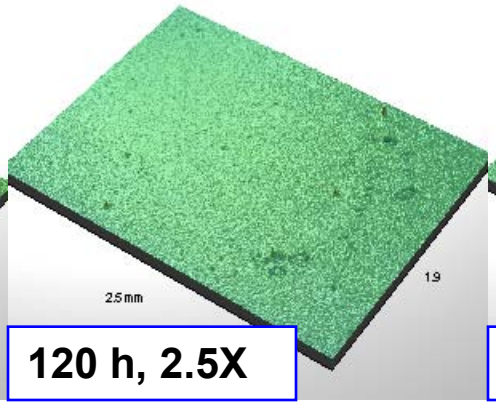



480 h, 50X

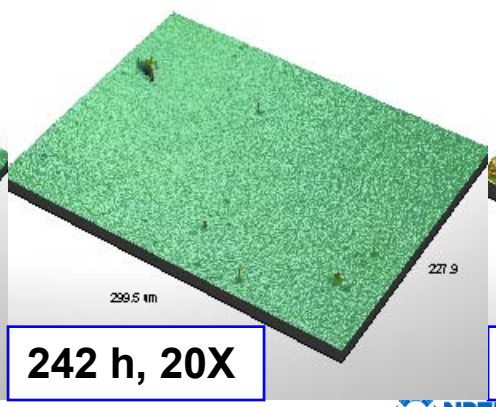
### Bi-layer i-/Al:ZnO (BZO), ~0.2 µm



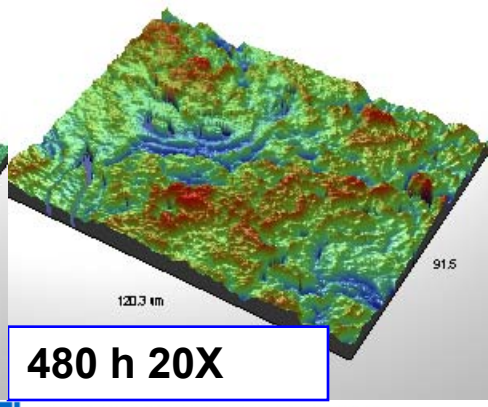

0 h, 20X




120 h, 2.5X

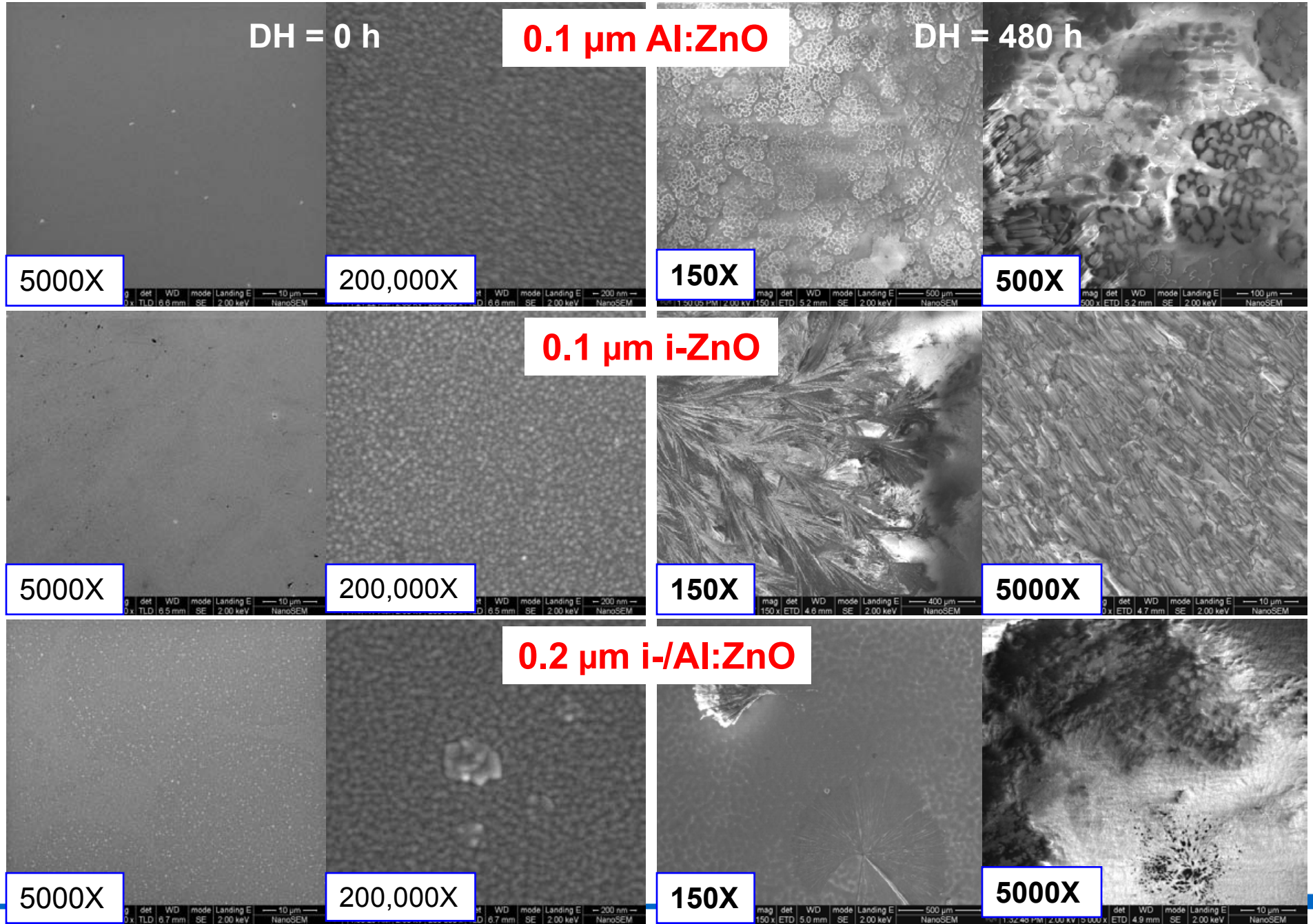



242 h, 20X

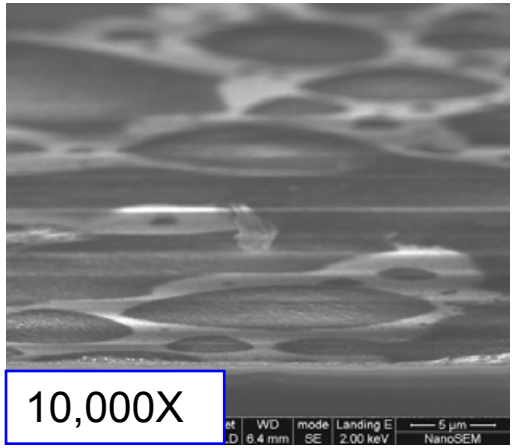


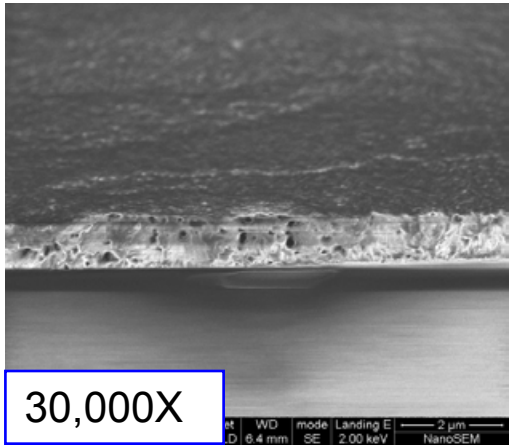

480 h 20X

# Surface Morphology Changes on ZnO Films (SEM)

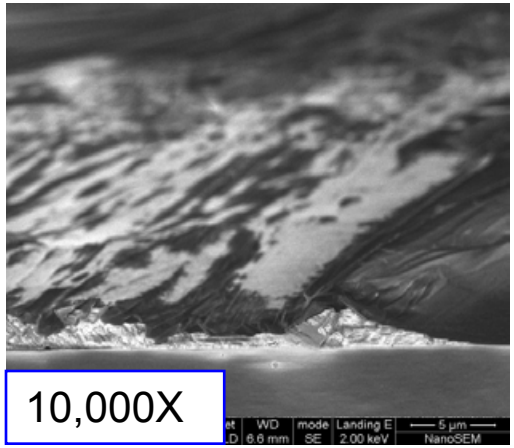


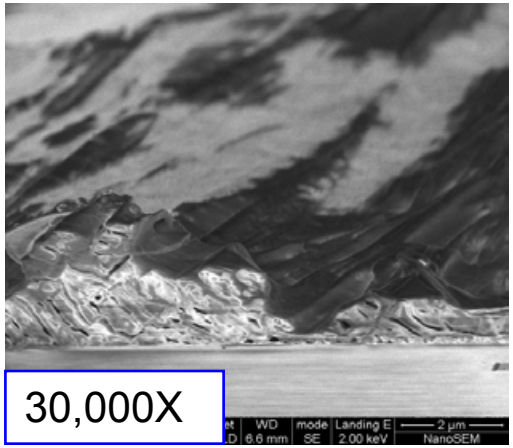
# ZnO Films at DH=480 h Became Porous & 10~20X Thicker (10° tilt SEM)



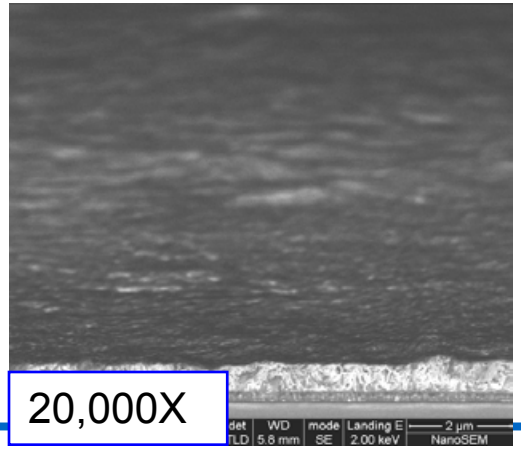



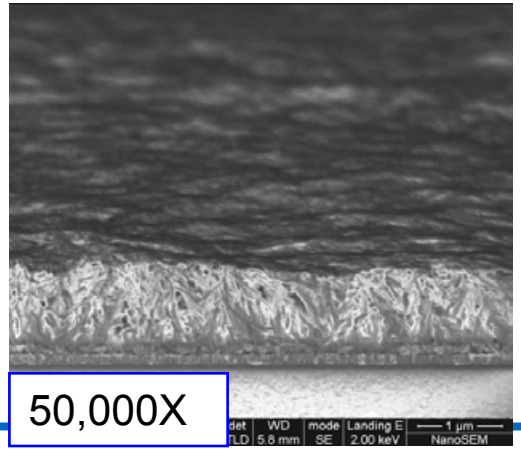

Al:ZnO 0.12 µm => ~1.5 µm, porous, ring-like features



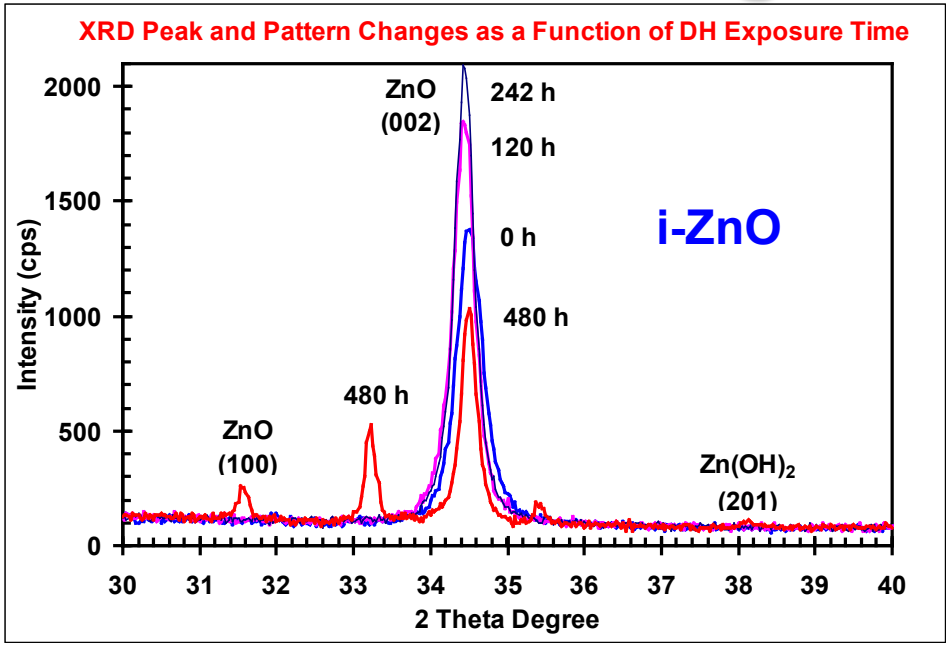

i-ZnO 0.1 µm => ~2 µm, porous, segregated (ditched)

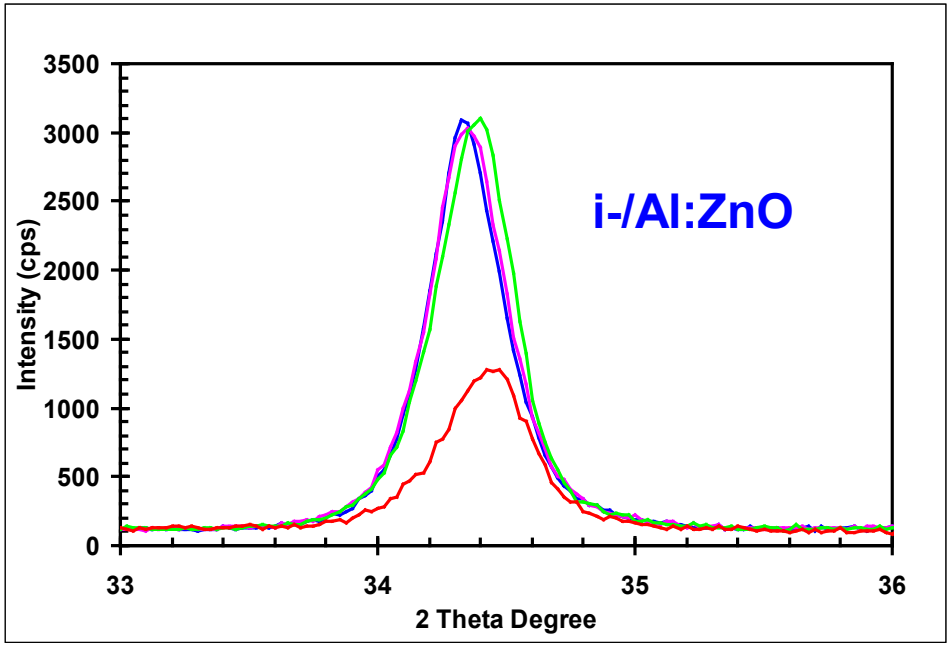


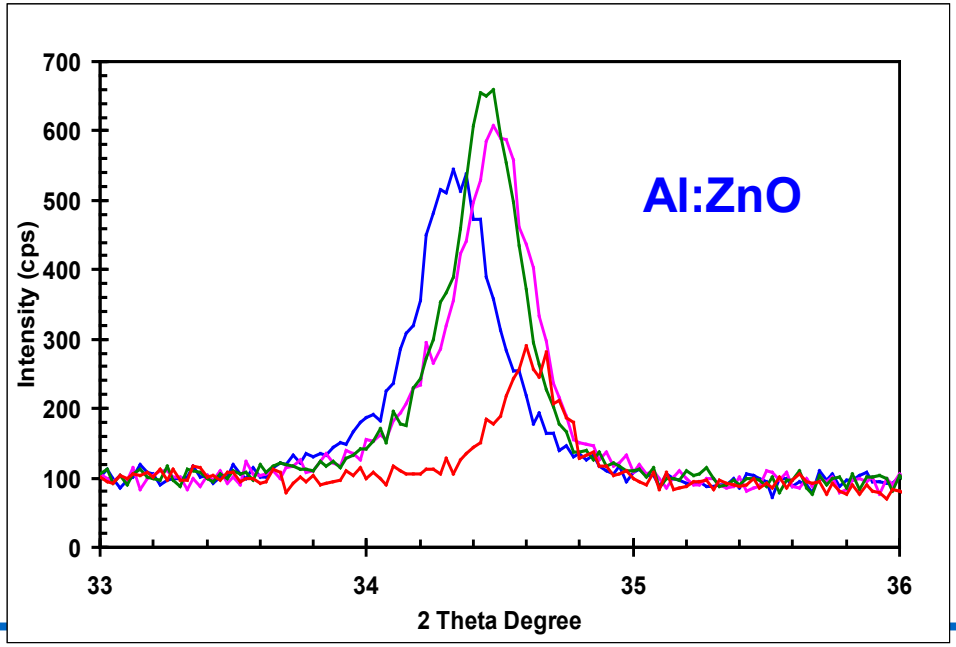



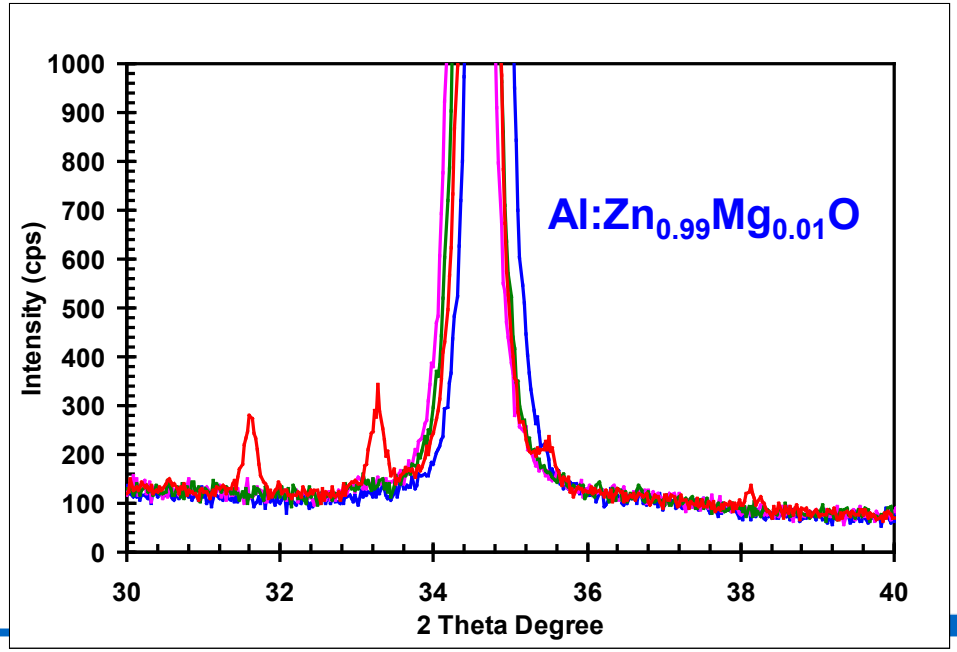

i-/Al:ZnO 0.2 µm => ~2 µm, porous, two layers

# Structural Degradation of ZnO in DH

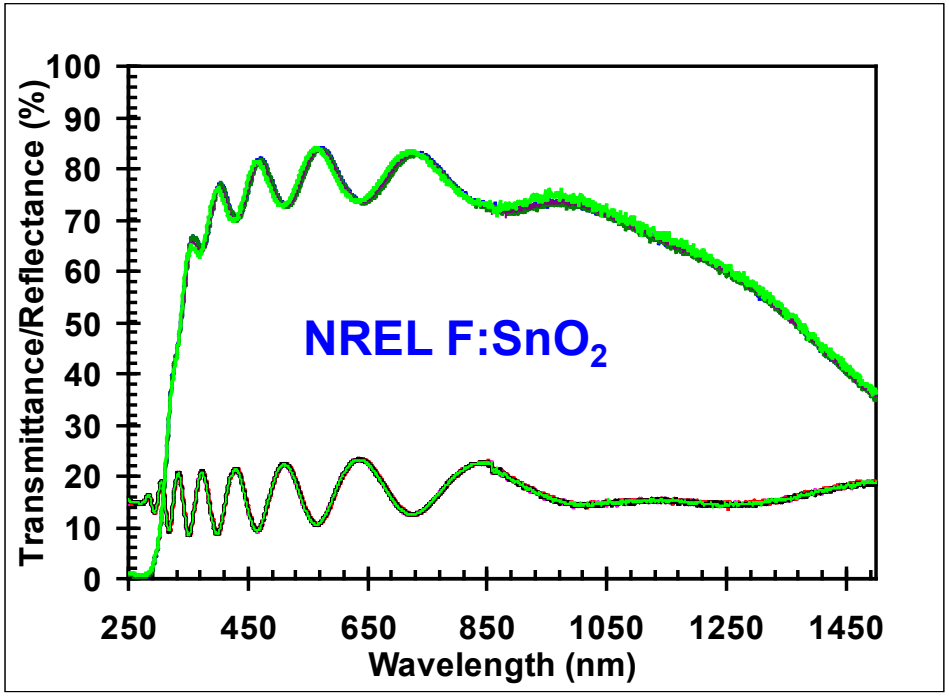


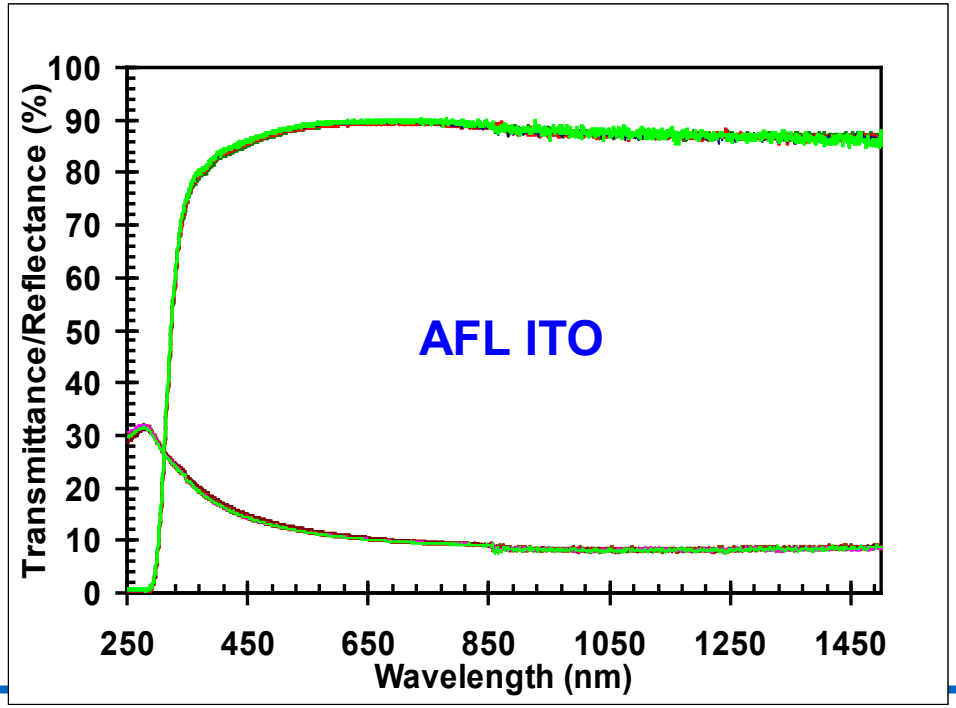



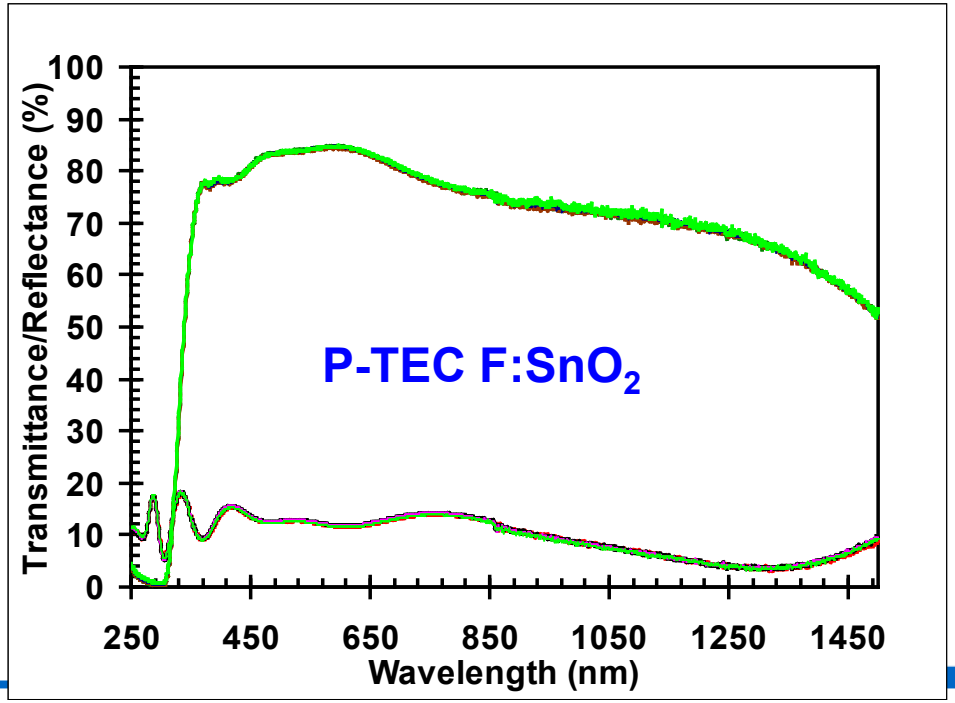



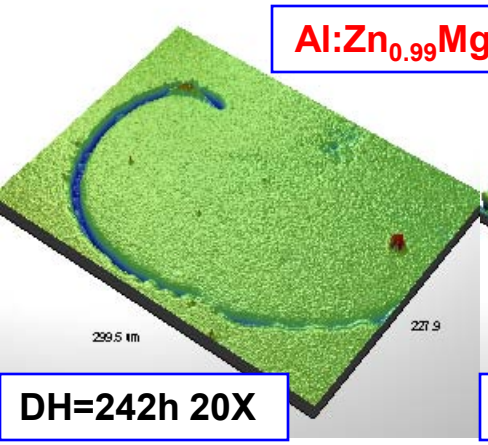
# "Apparent" Optical Stability of ITO & $F:SnO_2$ Coatings at DH = 480 h



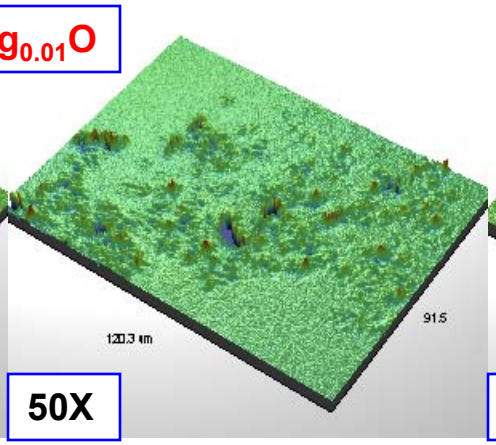



# More Morphological Degradations

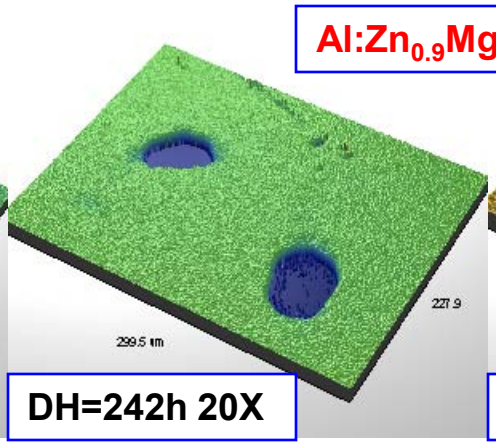



$Al:Zn_{0.99}Mg_{0.01}O$

DH=242h 20X

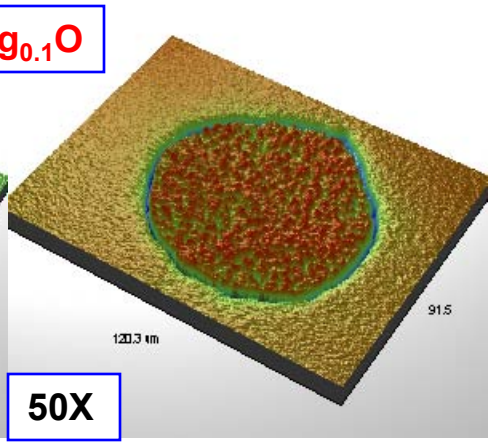



50X

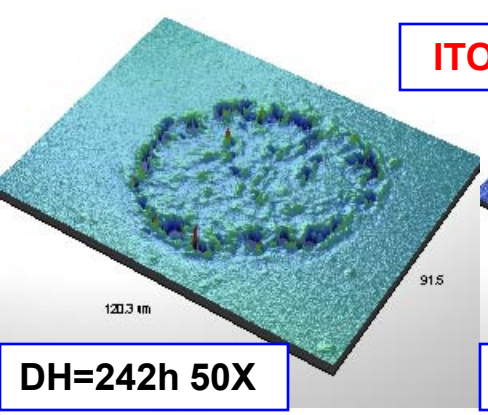



$Al:Zn_{0.9}Mg_{0.1}O$

DH=242h 20X

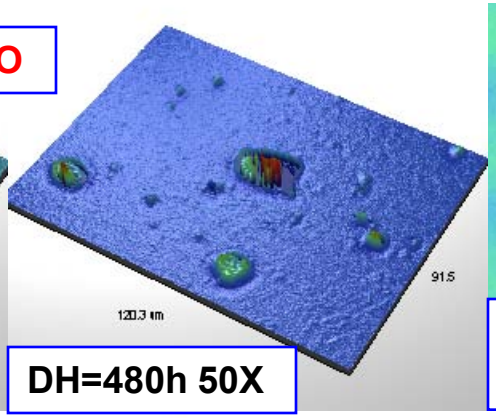



50X

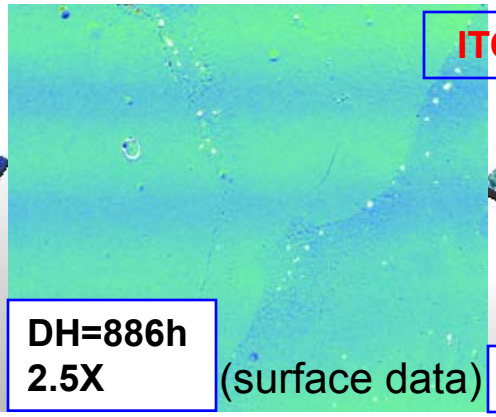



ITO

DH=242h 50X

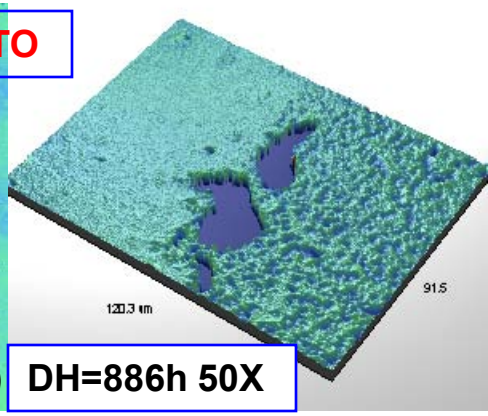



DH=480h 50X

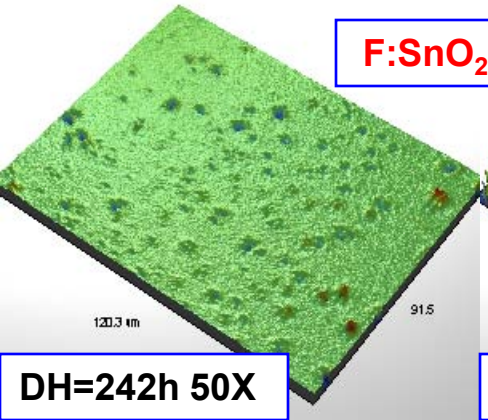


ITO

DH=886h 2.5X (surface data)

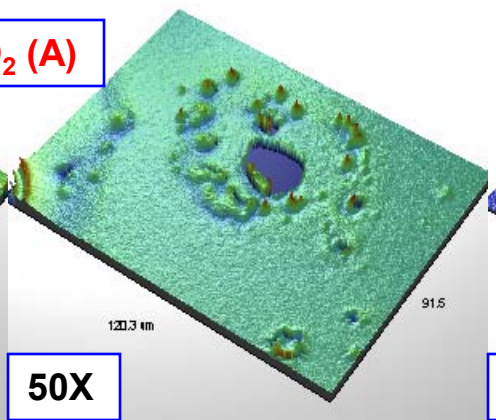



DH=886h 50X

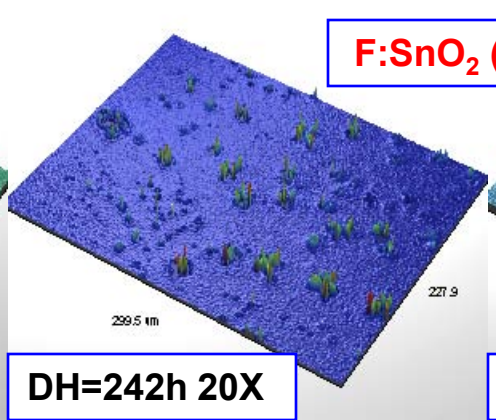



$F:SnO_2$ (A)

DH=242h 50X

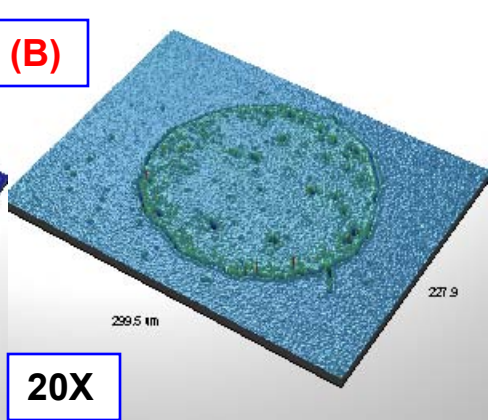



50X




$F:SnO_2$ (B)

DH=242h 20X




20X

# Electrical Degradation

## Degradation Rate:

**ZnO >> ITO > $F:SnO_2$**

## For Al-doped ZnO:

- Thickness Effect
- Substrate Temperature Effect
- "Dry-out" Effect
- Transient Effect

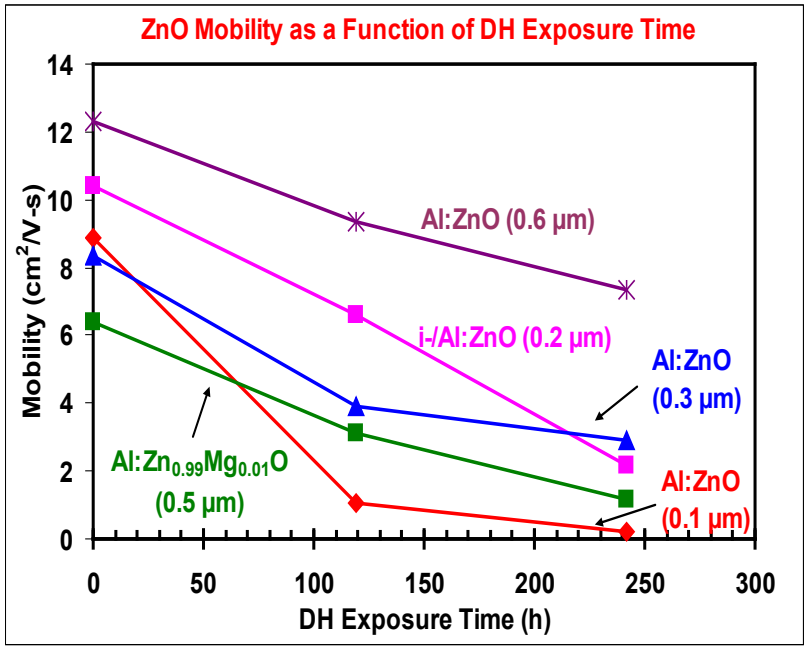



**Table 1. Sample Data and Sheet Resistance Changes upon Damp Heat Exposure**

| Sample ID | IZO-11 | AZO-21 | BZO-31 | AZO-383 | AZO-471 | AZO-501 | AZO-681 | AFL-1 | L6A3-1 | P-TCO1 | P-TEC3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition | int.-ZnO | Al:ZnO | i-/Al:ZnO | Al:ZnO | Al:ZnO | Al:ZnO | Al:ZnO | Sn:In2O3 | F:SnO2 | F:SnO2 | F:SnO2 |
| MgO added | 0% | 0% | 0% | 0% | 1% | 10% | 0% | | | | |
| Dep. $T_{sub}$ (°C) | Ambient | Ambient | Ambient | Ambient | 100 | 100 | 100 | N/A | N/A | N/A | N/A |
| Thickness (µm) | 0.1 | 0.1 | 0.2 | 0.3 | 0.5 | 0.5 | 0.6 | N/A | 0.5~0.6 | 0.26 | N/A |
| DH Time (h) | Rsh (ohm/sq) | | | | | | | | | | |
| 0 | HR* | 85.71 | 64.03 | 68.19 | 73.30 | HR* | 29.34 | 83.00 | 8.30 | 17.92 | 12.53 |
| 120 | | 967.00 | 107.70 | 155.60 | 165.50 | | 39.11 | 77.87 | 7.98 | 17.15 | 12.82 |
| 242 | | 15110.00 | 510.50 | 236.10 | 272.50 | | 50.10 | 82.05 | 7.80 | 17.42 | 12.66 |
| 480 | | HR* | HR* | HR* | HR* | | HR* | 83.20 | 8.00 | 17.82 | 12.77 |
| 886 | HR*: Highly resistive | | | | | | | 84.34 | 8.24 | 17.38 | 12.69 |
| Deg. Rate [(ohm/sq)/h] | | 6.21E+1 | 1.84E+0 | 6.94E-1 | 8.23E-1 | | 8.58E-2 | 1.51E-3 | -6.99E-5 | -6.09E-4 | 1.80E-4 |

# Damp Heat Degraded CIGSSe Mini-Modules

R. Feist et al., 33 IEEE PVSC, May 2008

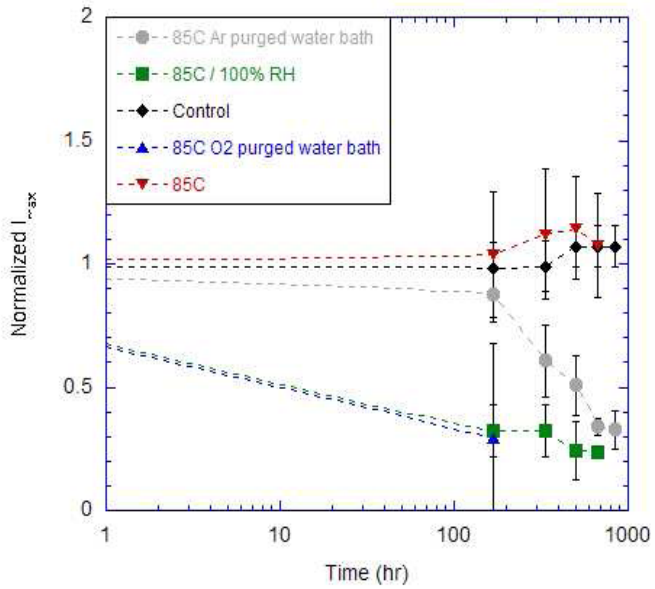



Fig. 2 Normalized $I_{max}$ from SSI cells exposed to various environments.

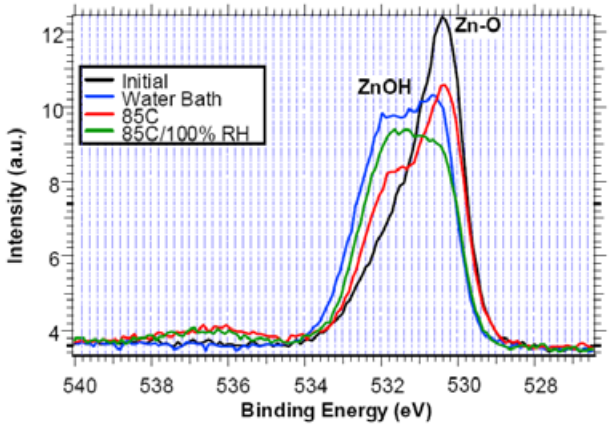
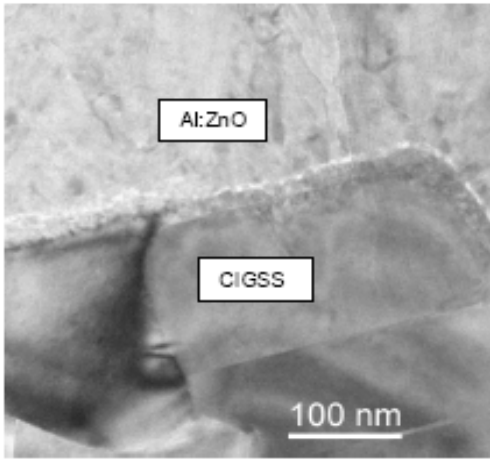



Fig. 8 XPS oxygen spectra of the sample surfaces.




TEM cross-section of as-received SSI cell.

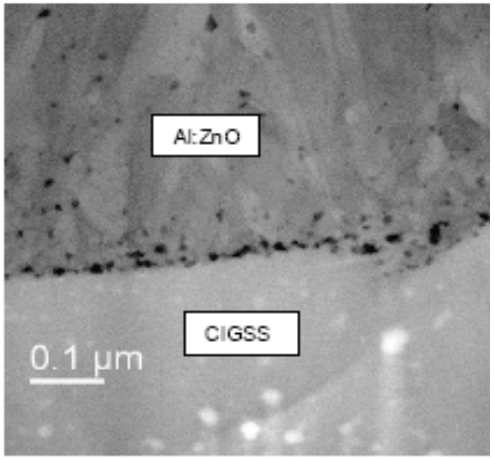



Fig. 5 TEM cross-section of SSI cell after exposure t
85°C water bath

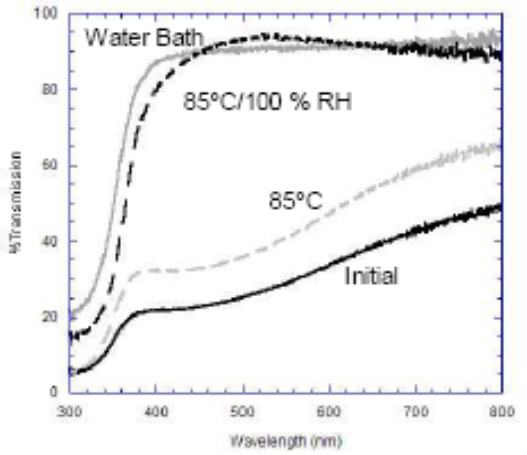



Fig. 6 UV/Vis of Al:ZnO samples initially and after 24 hr exposure to 85°C, 85°C/100% RH, and a water bath.

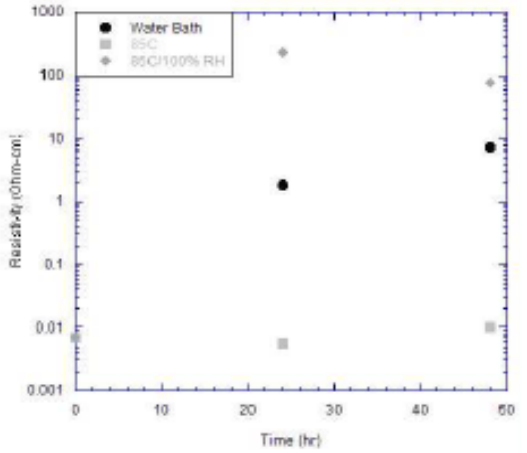
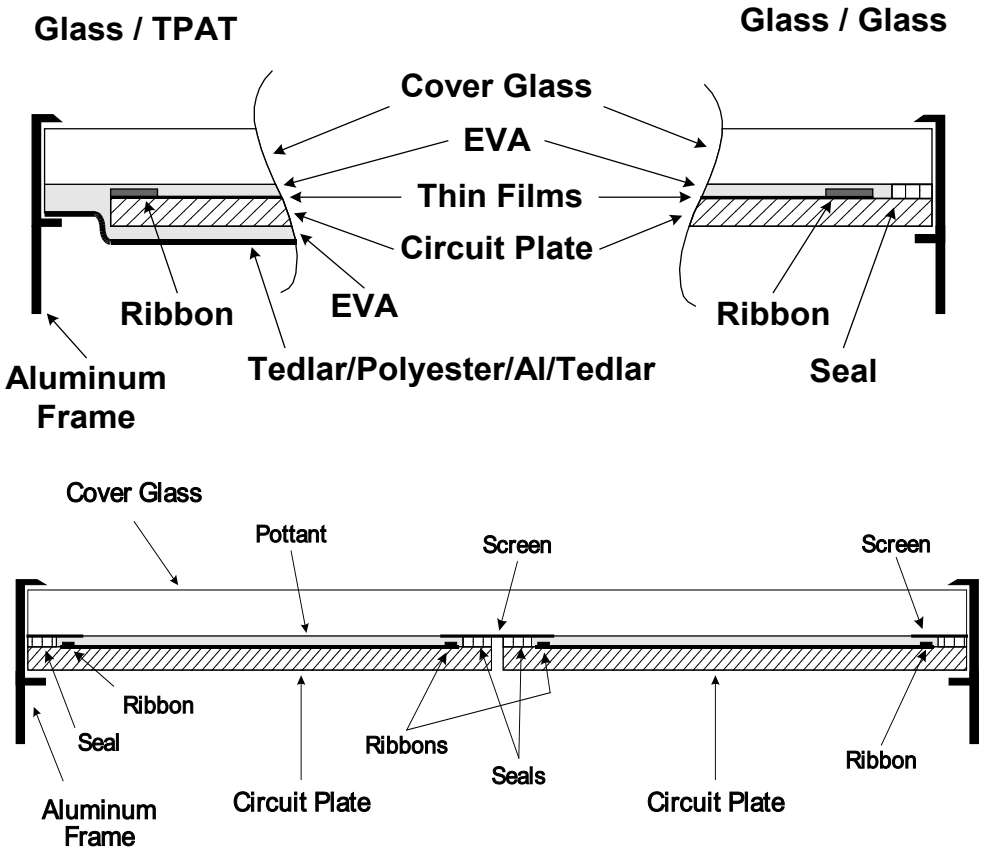



Fig. 7 Resistivity of Al:ZnO films after exposure to 85°C, 85°C/100% RH, and a water bath.

# Impact on Thin-Film PV Encapsulation and Construction

- More stringent requirements than c-Si PV
- Thin-film PV modules are mostly limited to glass/glass construction; some, e.g., CdTe and CIGS, with desiccant edge sealant to help block moisture ingress.
- Only a few flexible thin film modules (e.g., Uni-Solar's a-Si with ITO) have passed the damp heat (85°C, 85%RH, 1000h) qualification test.

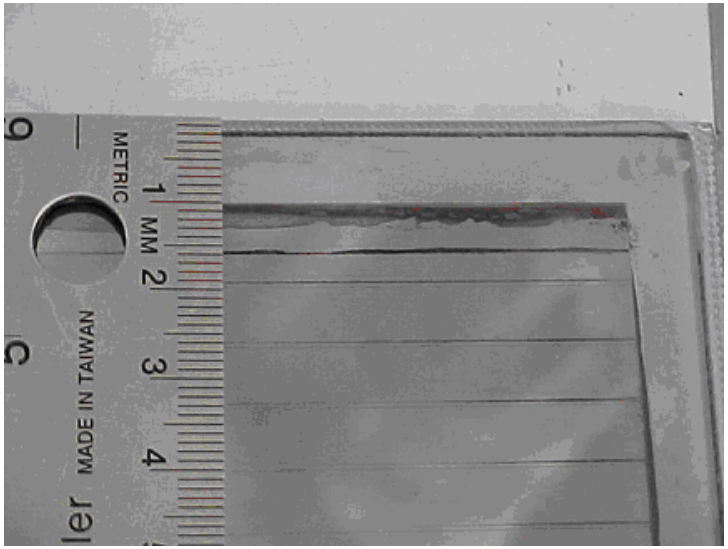
# CIGS with desiccant edge sealant




**Siemens Solar's "TPAT" and "glass/glass" package and ST80 CIGS codule designs.**

Dale E. Tarrant, PVMaT QR, 8/2004

**Passed 85/85 1000 h, but …**




**Corrosion** at the corner of a glass/glass laminate after 3000 h of damp heat exposure. **The majority of the test modules failed at 4000 h.**

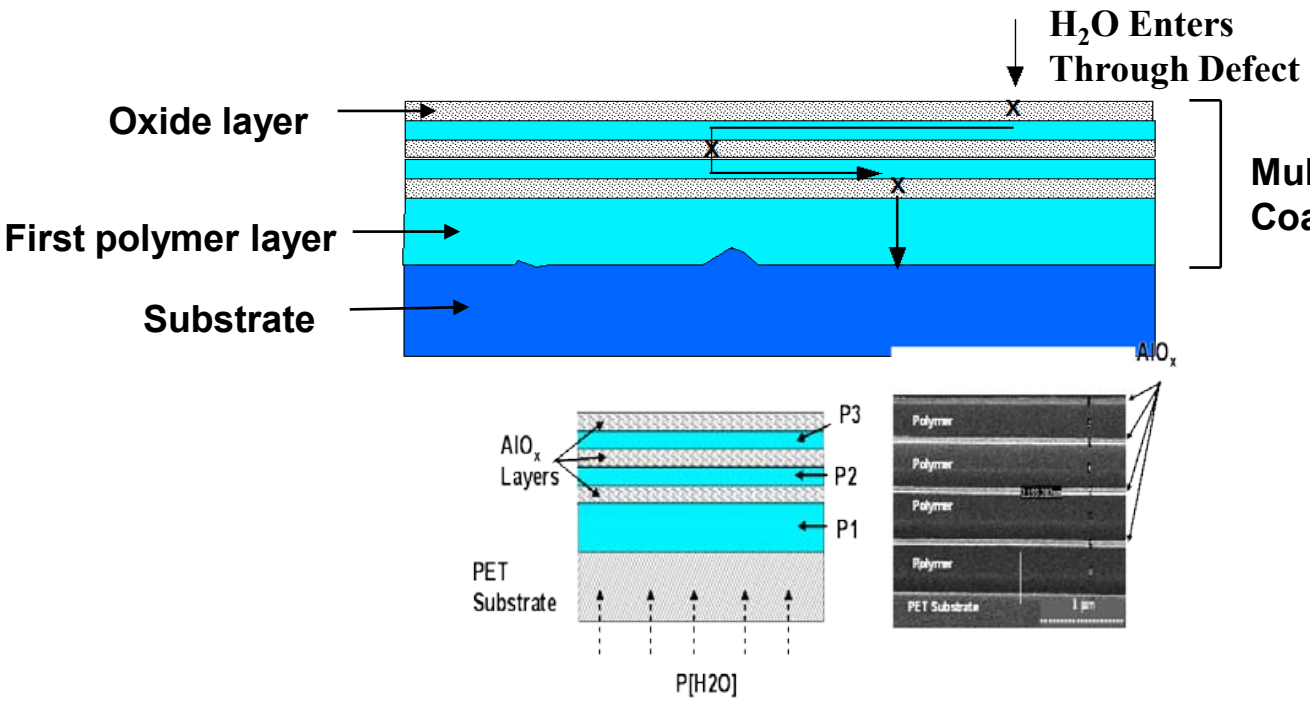
# Solutions Being Investigated

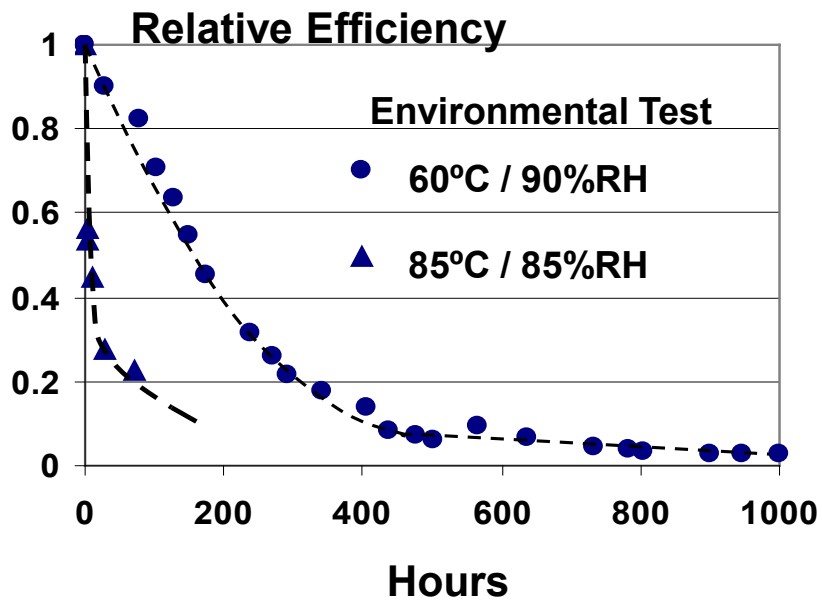
## CIGS, a-Si, and OPV (rigid/flexible package)

- Use ITO to replace Al-doped ZnO
- more DH-stable TCOs - InZnO, InGaZnO (NREL)
- Mitigation ZnO with Barrier Coating
  - -- Multilayer polymer/$Al_2O_3$ (PNNL)
    - -- CIGS mini-modules passed DH 1000 h test
  - -- Chemical with/without SiOxNy (NREL)
  - -- Other MO protective layers (NREL)
- Moisture-blocking polymeric topcover

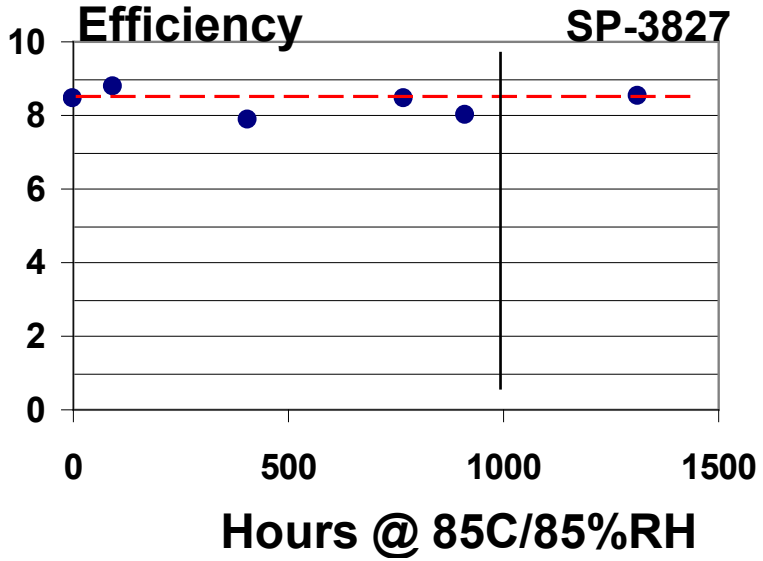
L. Olsen, SPIE PV, 8/2008

# PNNL's Multilayer Moisture Barrier




Uncoated CIGS Cells with ZnO TCO's




Laminated SoloPower mini-module, 25 $cm^2$, on flexible metal foil

# Summary

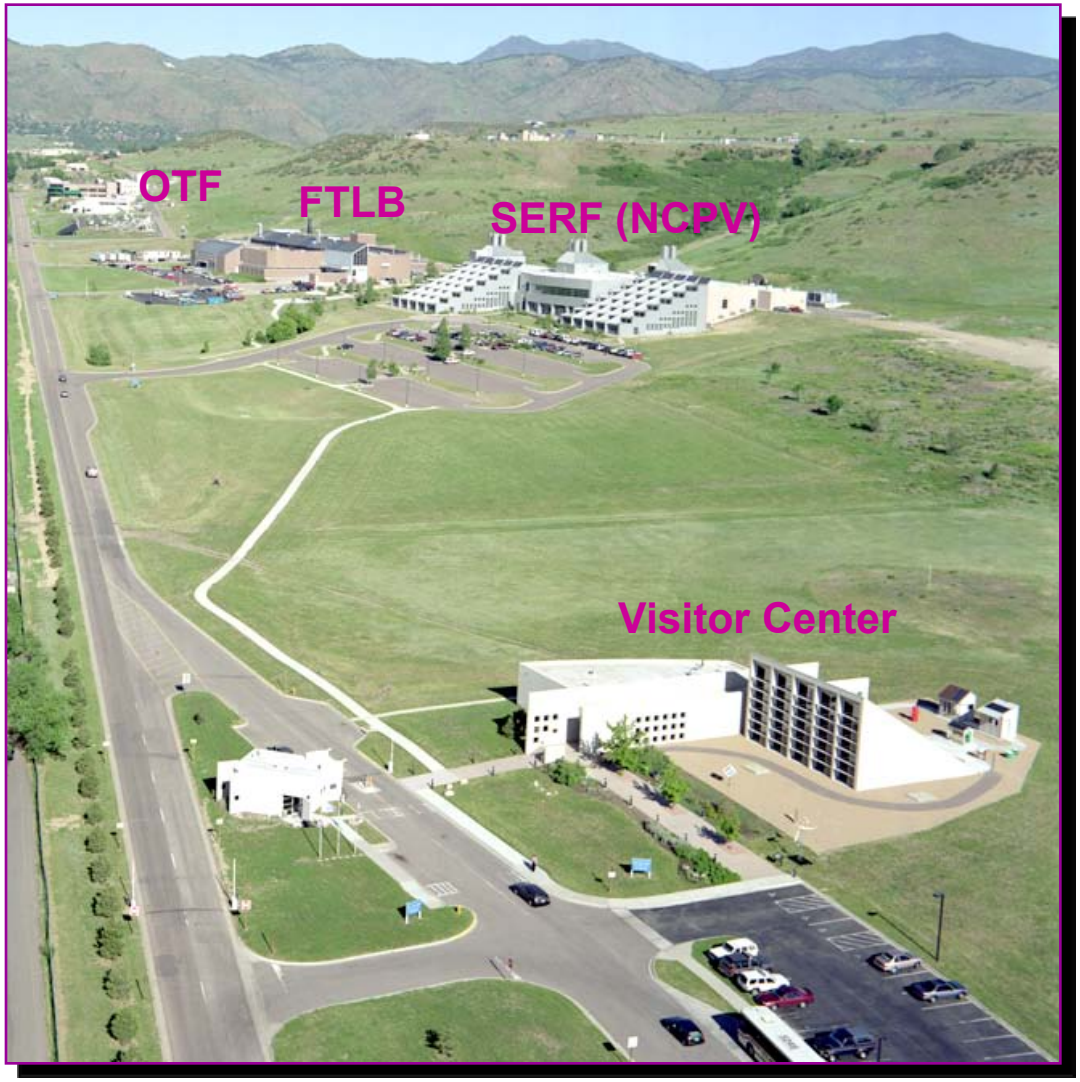
- Degradation in the optical, electrical, and structural properties of ZnO, ITO, and F:$SnO_2$ on glass substrates upon direct damp heat exposures.

  Degradation Rate in DH: ZnO >> ITO > F:$SnO_2$

- Instability of TCO, especially ZnO-based contact electrodes, (and absorber), imposes stringent requirements on thin-film module encapsulation and construction to minimize or eliminate the detrimental effects of moisture ingress.

- New DH-stable TCOs and moisture-blocking barrier or mitigation methods are under developments.

# NREL's 300-Acre South Table Mountain Site




- **NREL:** National Renewable Energy Laboratory
- **NCPV:** National Center for Photovoltaics (NREL+SNL)
- **SERF:** Solar Energy Research Facility (NCPV)
- **OTF:** Outdoors (+ Indoors) Test Facility for PV modules and systems
- **FTLB:** Field Test Laboratory Building (Biotech/Chemical)

1617 Cole Blvd.,
Golden, CO 80401, U.S.A.
http://www.nrel.gov/

# Solar Energy Research Facilities (SERF)

Science and Technology Facilities (STF)