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

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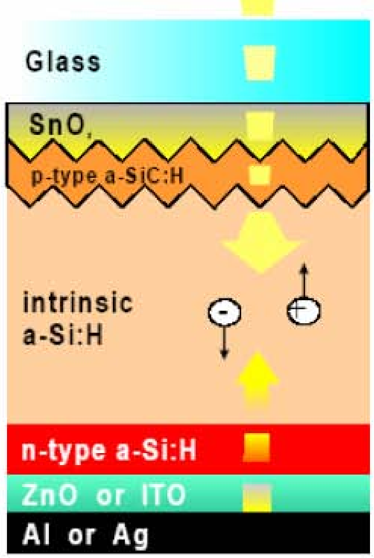
Outline

- **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**

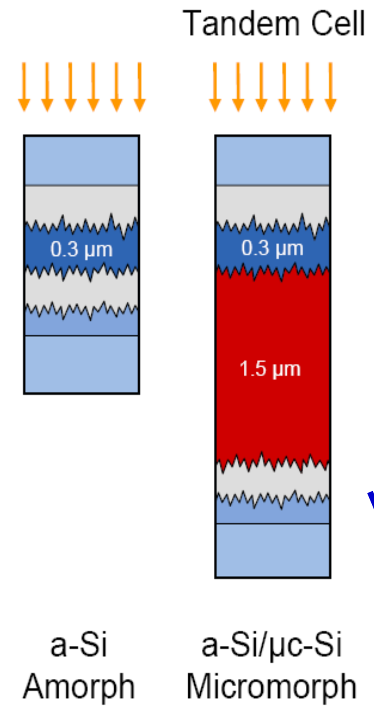
TCO in PV Applications

- 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.

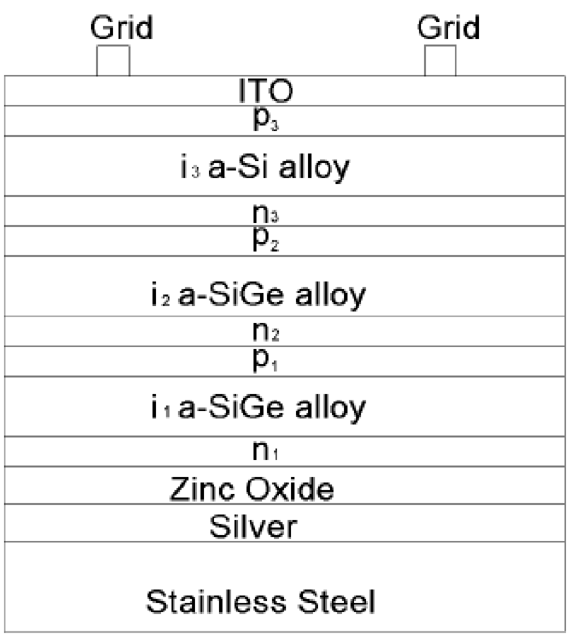
Example-1: ZnO, ITO, and SnO_2 in a-Si & a-Si/µc-Si micromorph PV



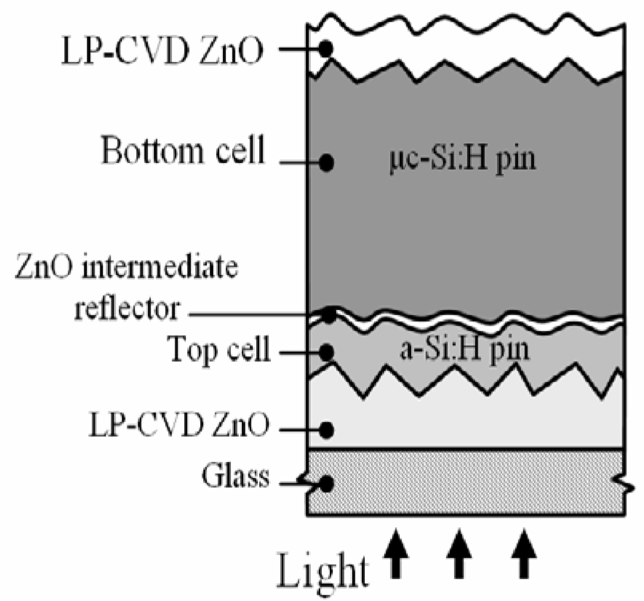
Single p-i-n junction a-Si Oerlikon Solar



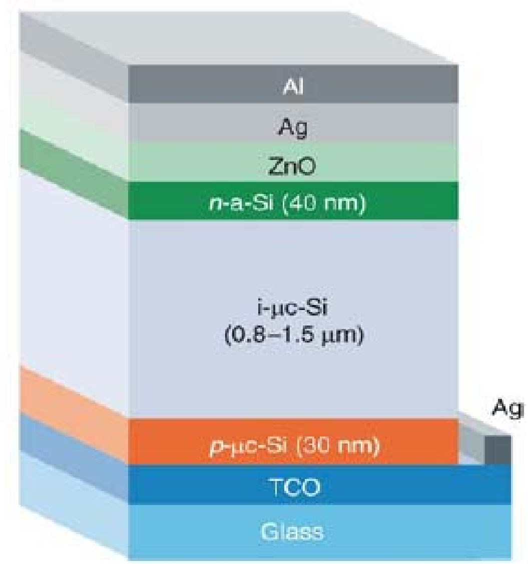
Sanyo Single junction p-i-n a-/µcSi



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



D. Domine et al., IMT, 2005



MRS BULLETIN • VOL. 32 • MARCH 2007

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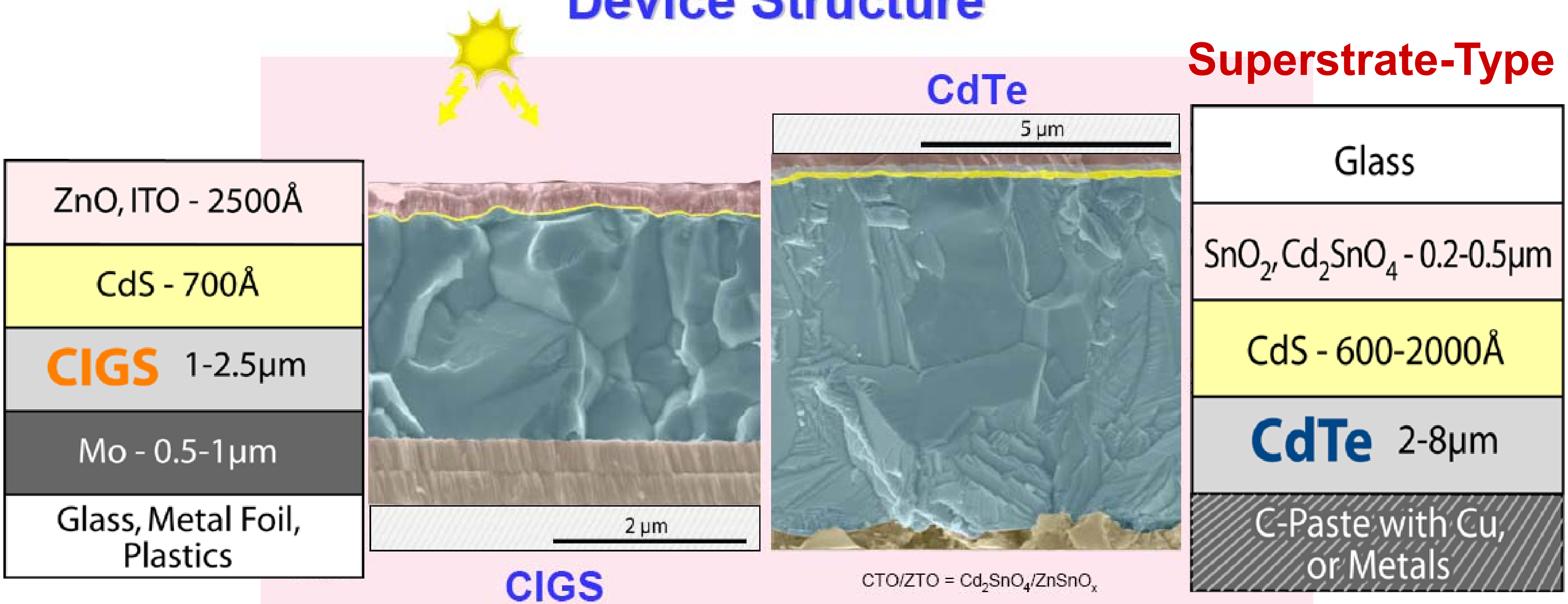
Example-2: ZnO, ITO, SnO_2, Cd_2SnO_4 in CIGS and CdTe PV

NREL's High Efficiency CIGS and CdTe Device Structure

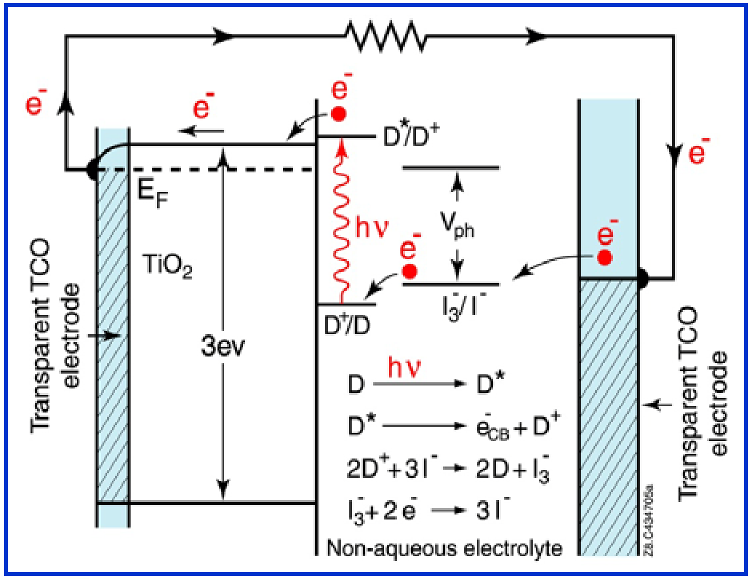


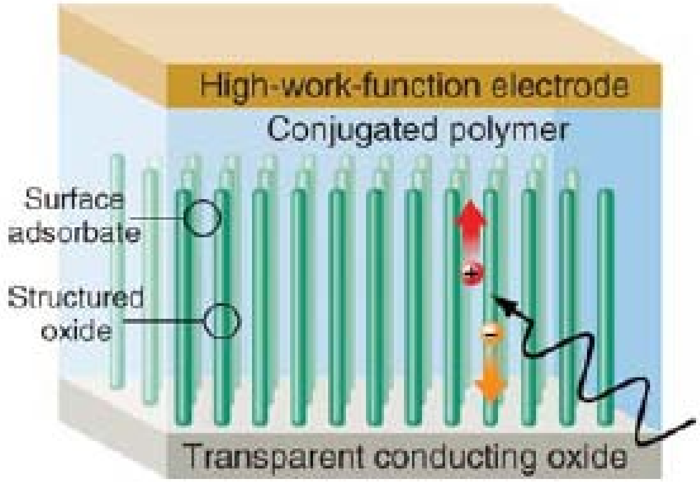
Substrate-Type

η = 19.9%

η = 16.5%

(Graetzel) Dye-Sensitized Solar Cell (DSSC)





Nanowire DSSC

Example-3:

Organic Solar Cell (OPV)

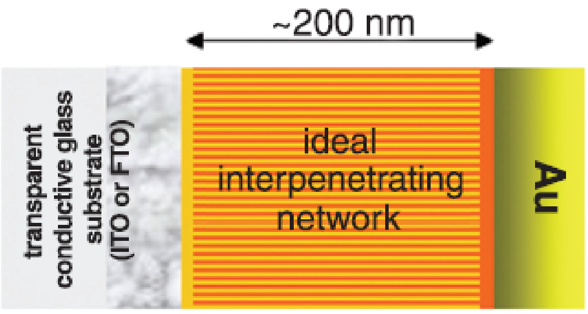
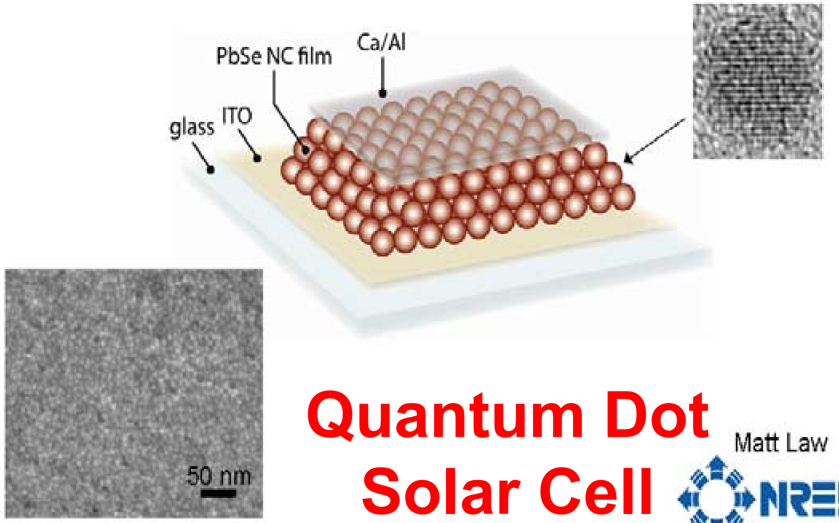


Fig. 6 Schematic of a hybrid solar cell with an ideal interpenetrating network consisting of highly aligned and ordered ZnO nanowires and an organic hole transporter material.



Quantum Dot Solar Cell

Matt Law

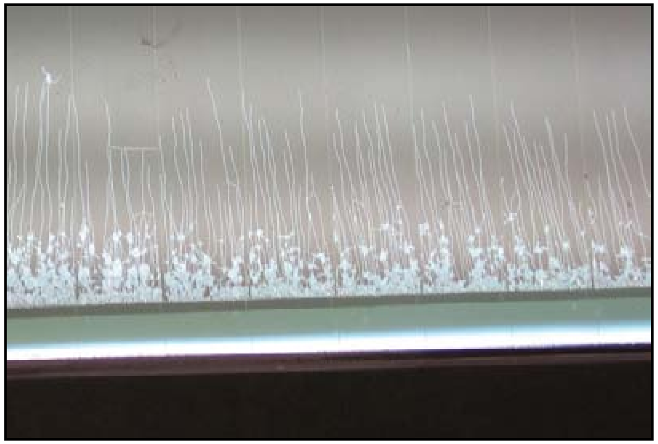
NREL

Stability Issues of Thin Film PV

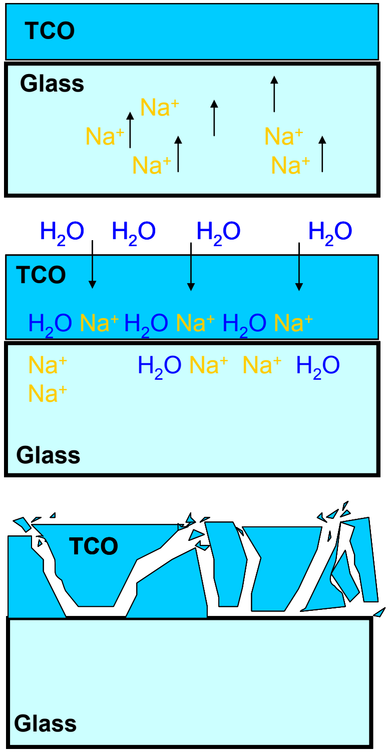
- **Two aspects: Absorber vs. TCO**
- **Absorber:** CIGS, CdTe, Organic (OPV)
  - sensitivity to moisture at elevated temperature.
- **TCO:** stability concerns as contact electrode or buffer layer or internal reflector
  - sensitivity to moisture and applied voltage at elevated temperature.

(This talk focuses only on TCO)

Corrosion



TCO Delamination



Negatively biased

K.W. Jansen, EPV, SPIE PV, 8/2008

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^{o}C/85%RH (IEC 61646)**
- **In DH with acetic acid vapor**
- **in a weatherometer (WOM) at 2.5 UV suns/60^{o}C/60%RH**

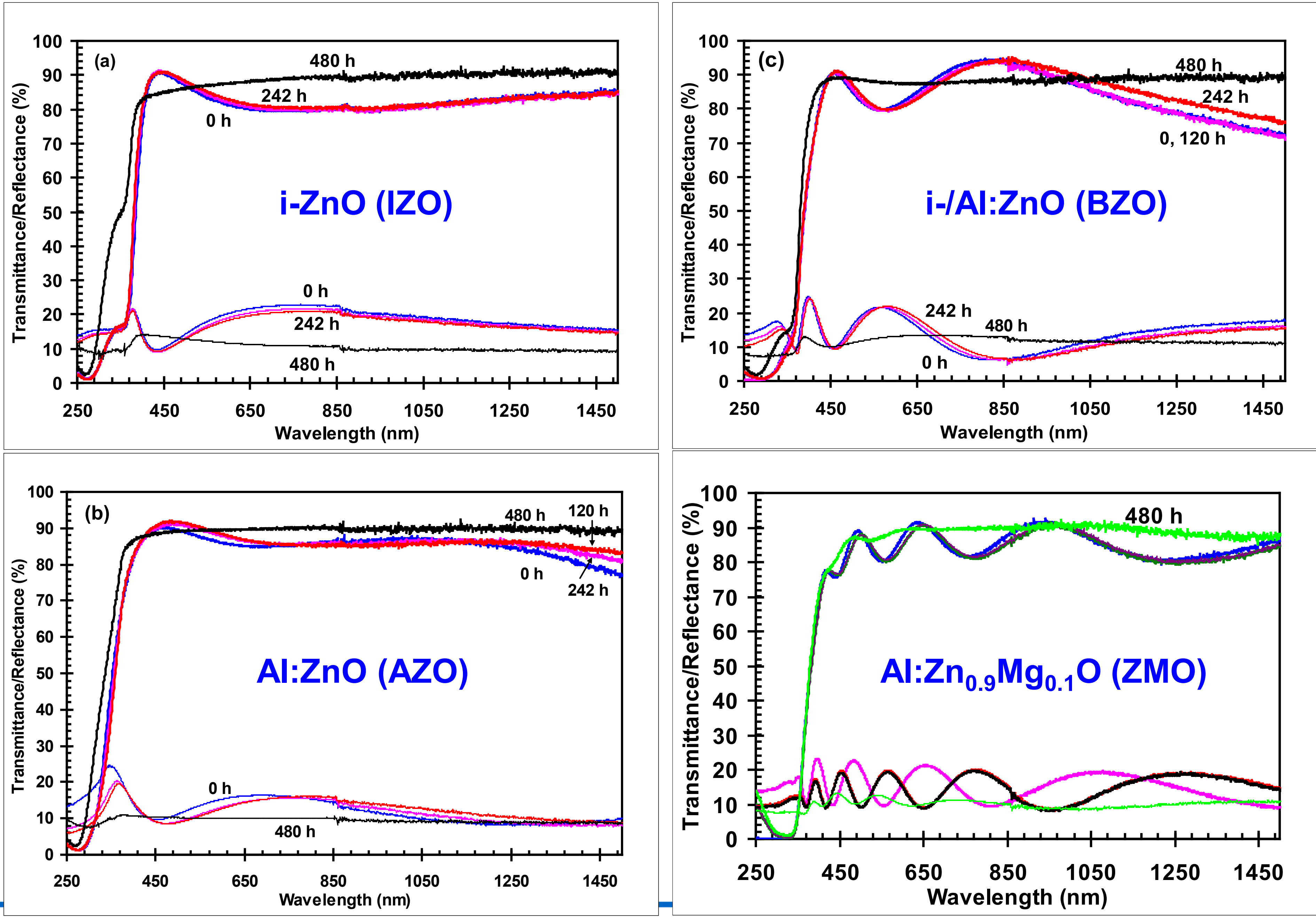
Characterization:

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

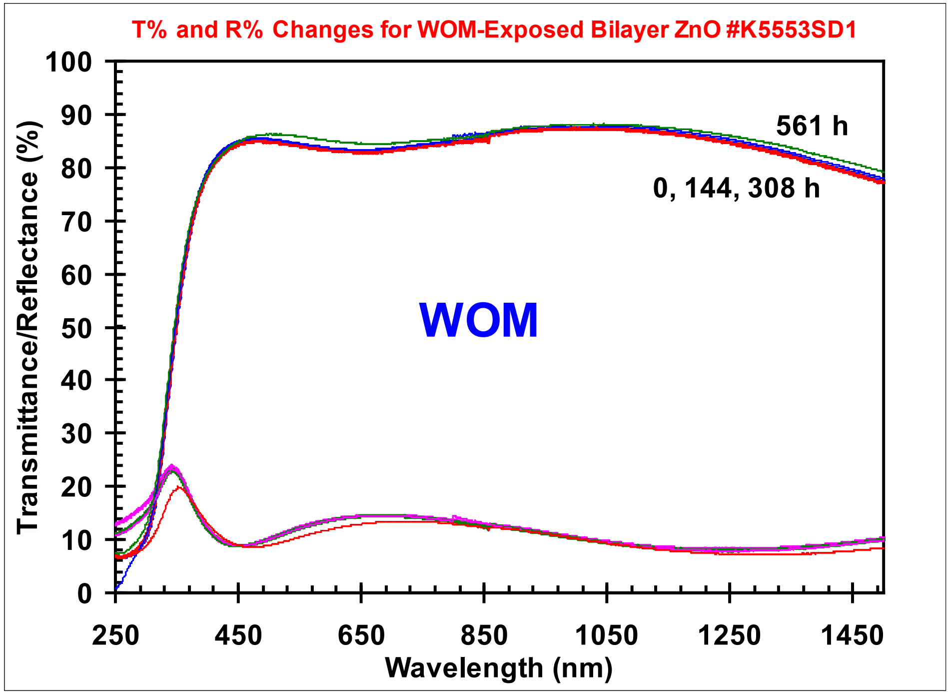
Atlas Ci4000 WOM

=> To identify degradation mechanism and quantify degradation rates

Optical Degradation of ZnO & ZMO in DH

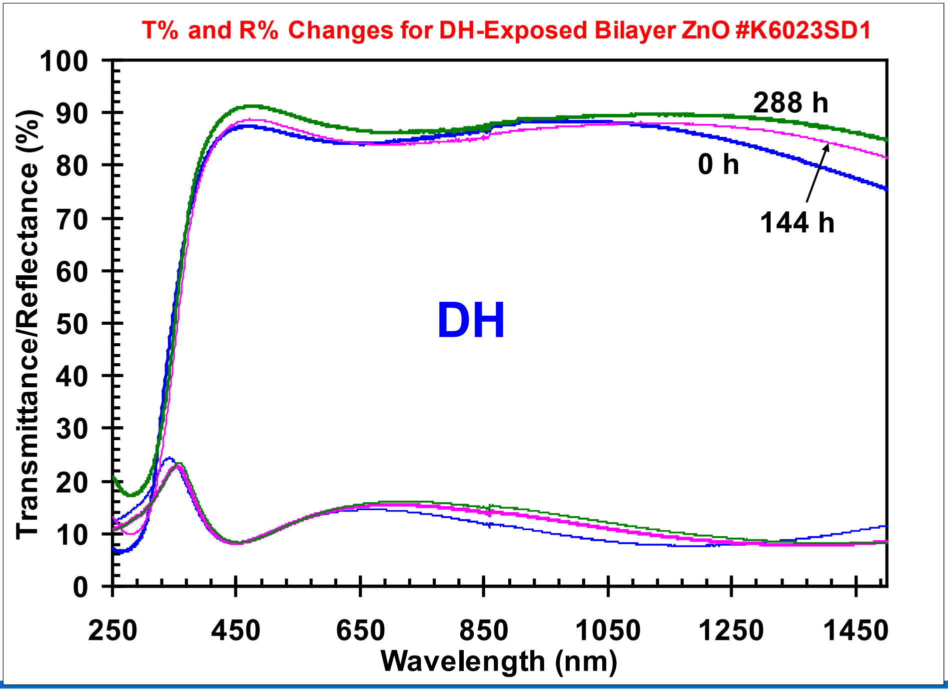


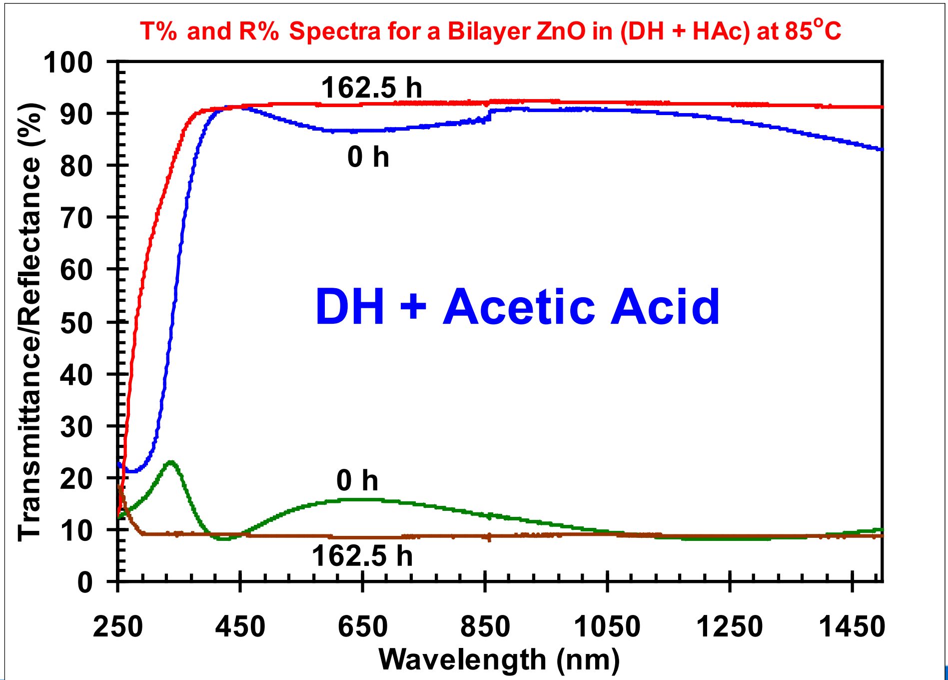
Optical Degradation of Bi-layer i-/Al:ZnO (BZO)



Degrading Effect:

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

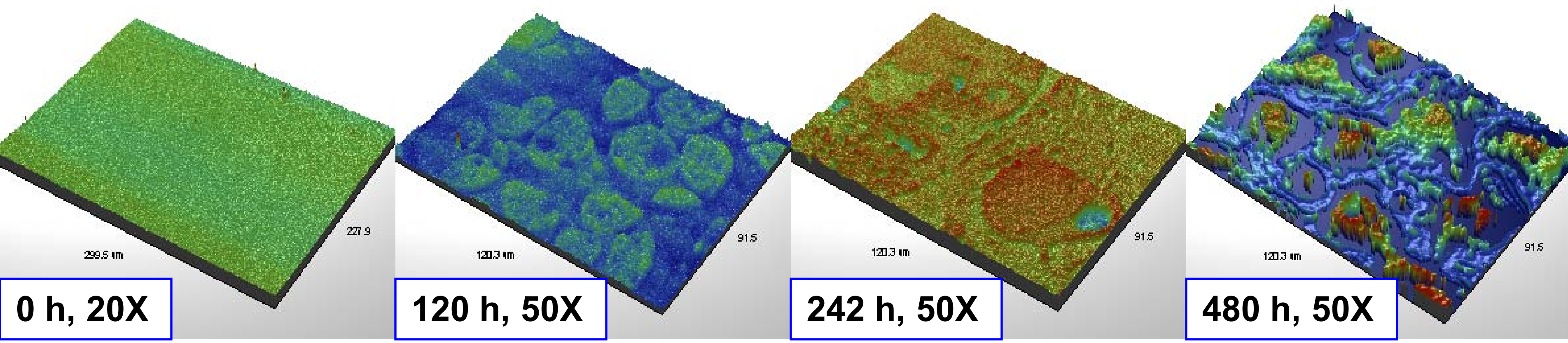




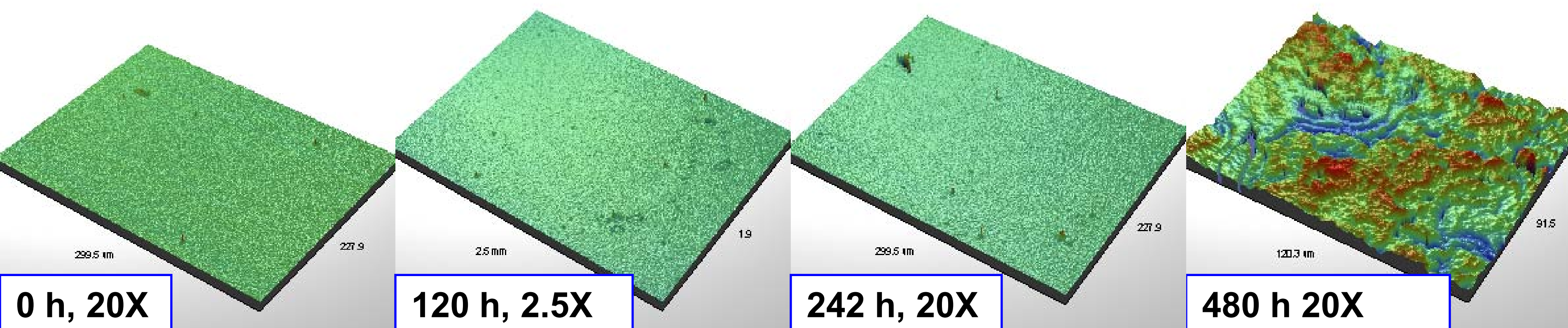
Surface Morphology Changes on Al:ZnO & i-/Al:ZnO upon DH Exposures

(WYKO Optical Interferometer)

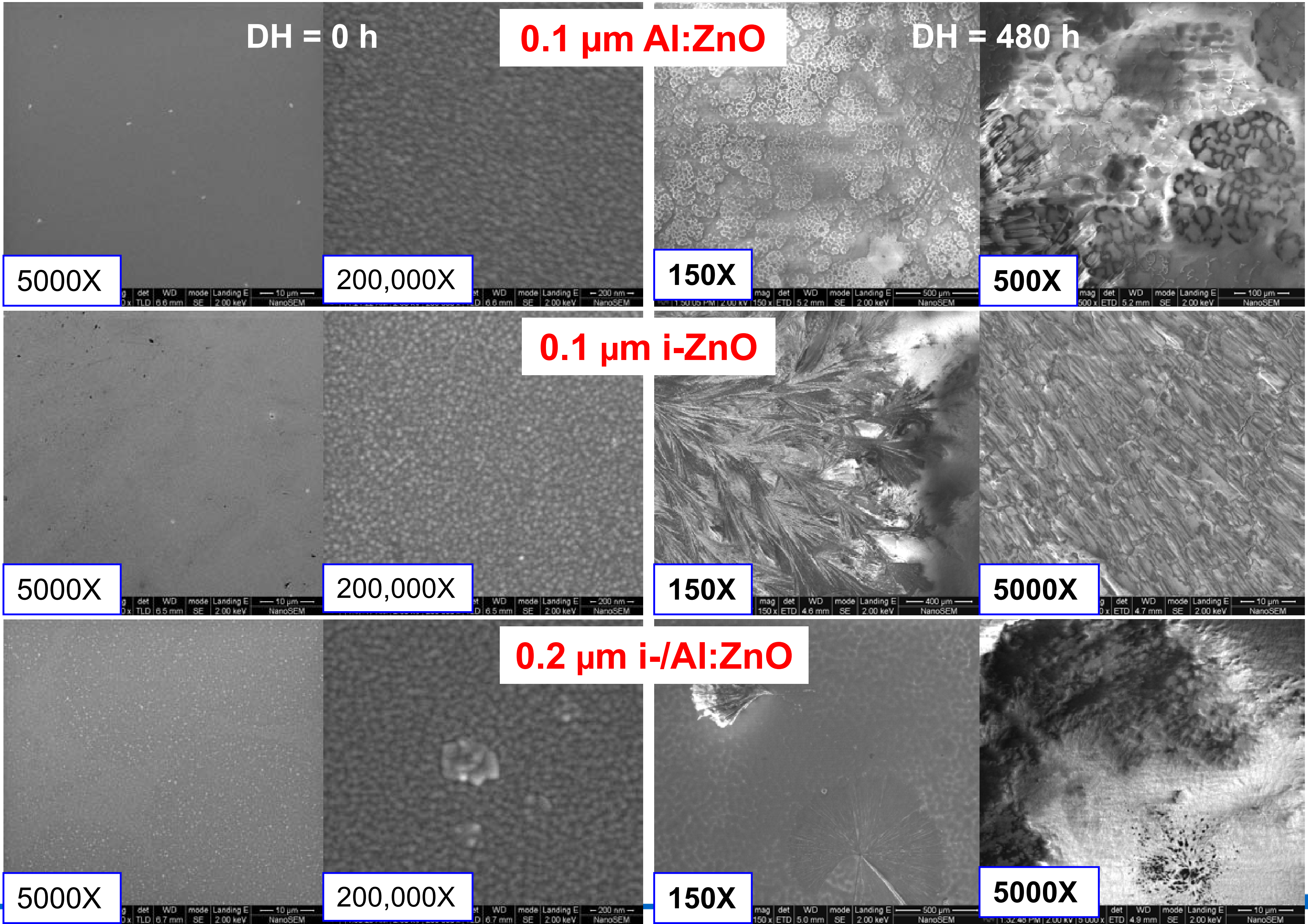
Single-layer Al:ZnO (AZO), ~0.1 μm



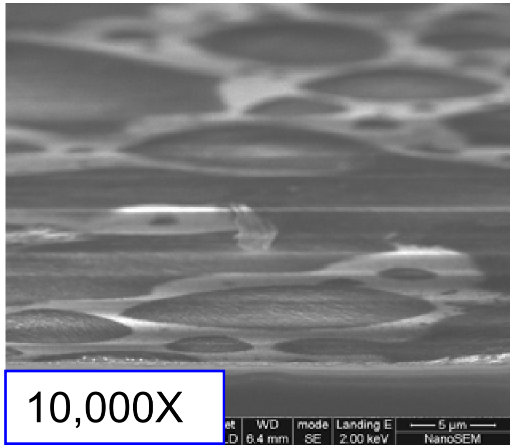
Bi-layer i-/Al:ZnO (BZO), ~0.2 μm

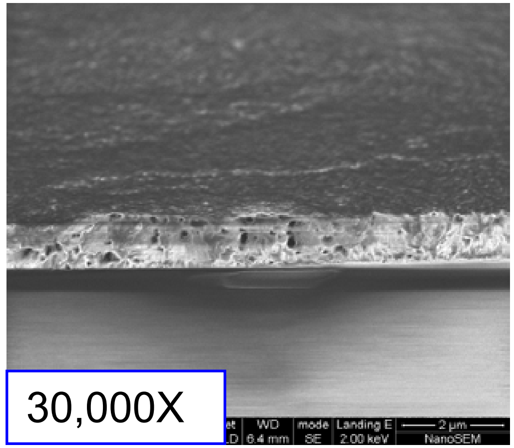


Surface Morphology Changes on ZnO Films (SEM)

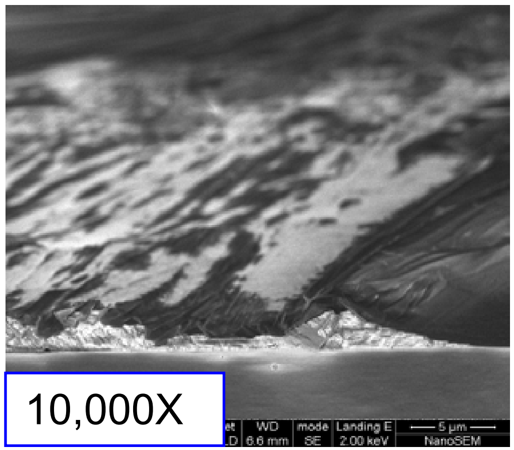


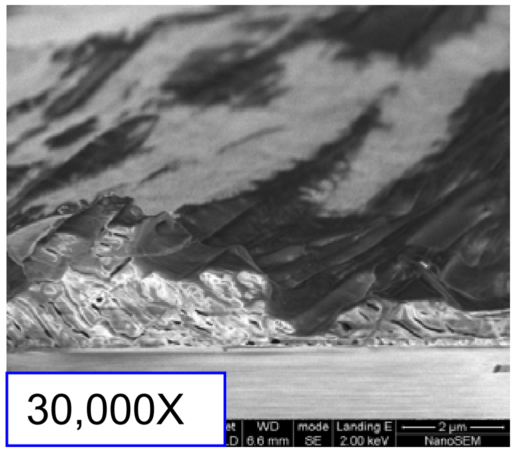
ZnO Films at DH=480 h Became Porous & 10~20X Thicker (10° tilt SEM)



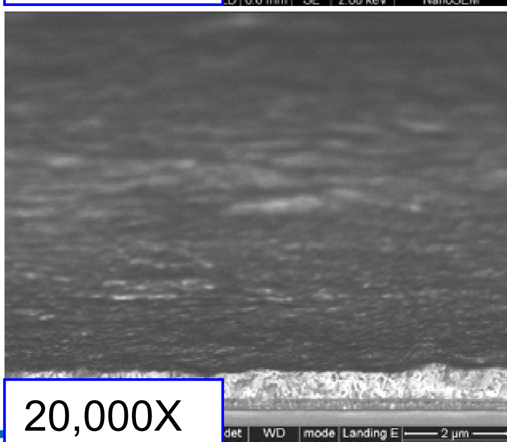


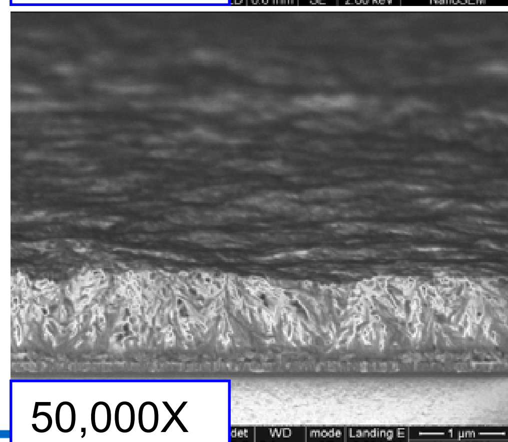
Al:ZnO 0.12 μm => ~1.5 μm, porous, ring-like features





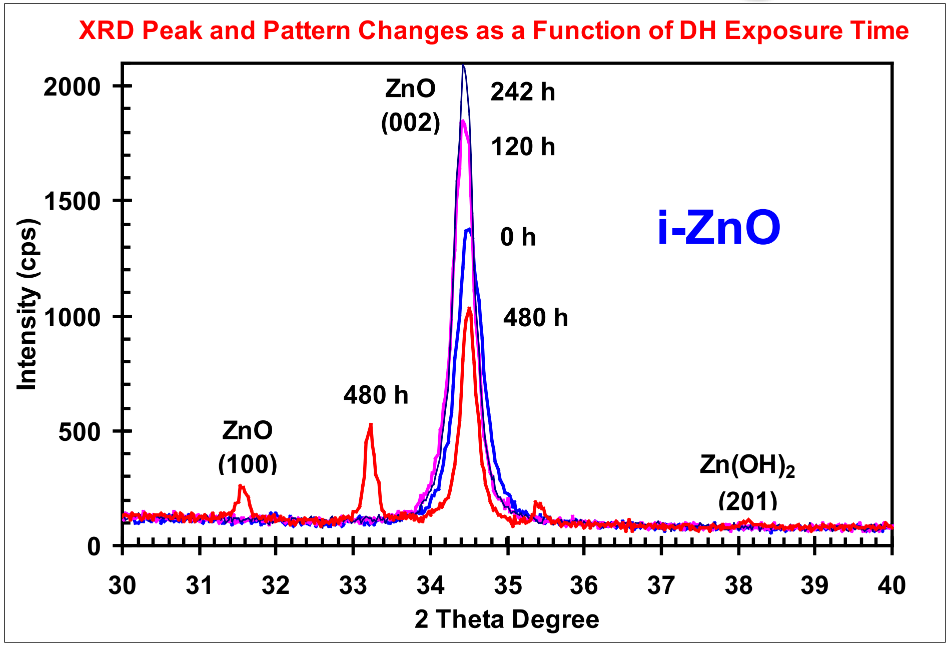
i-ZnO 0.1 μm => ~2 μm, porous, segregated (ditched)

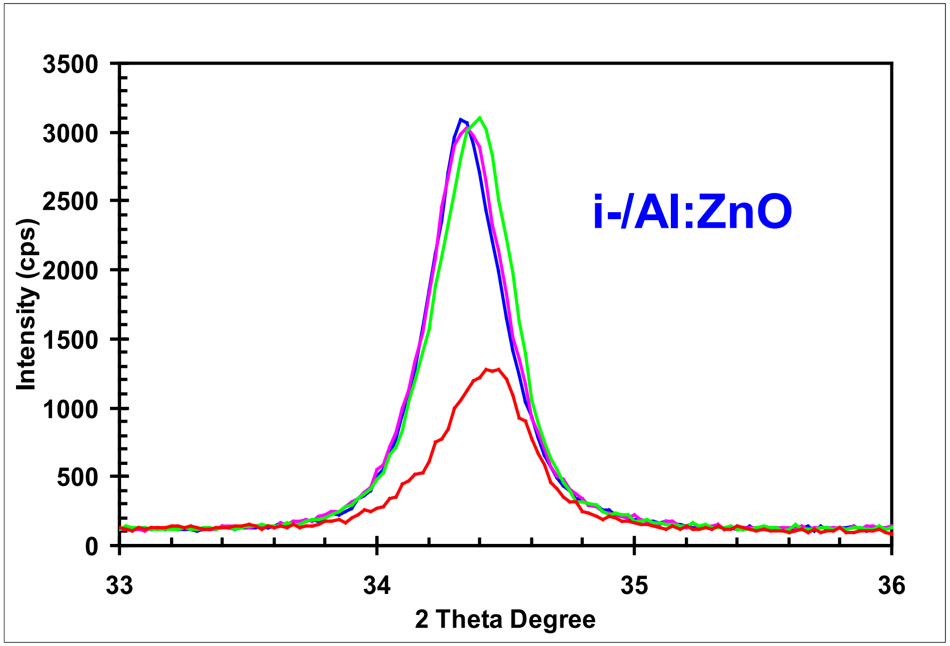


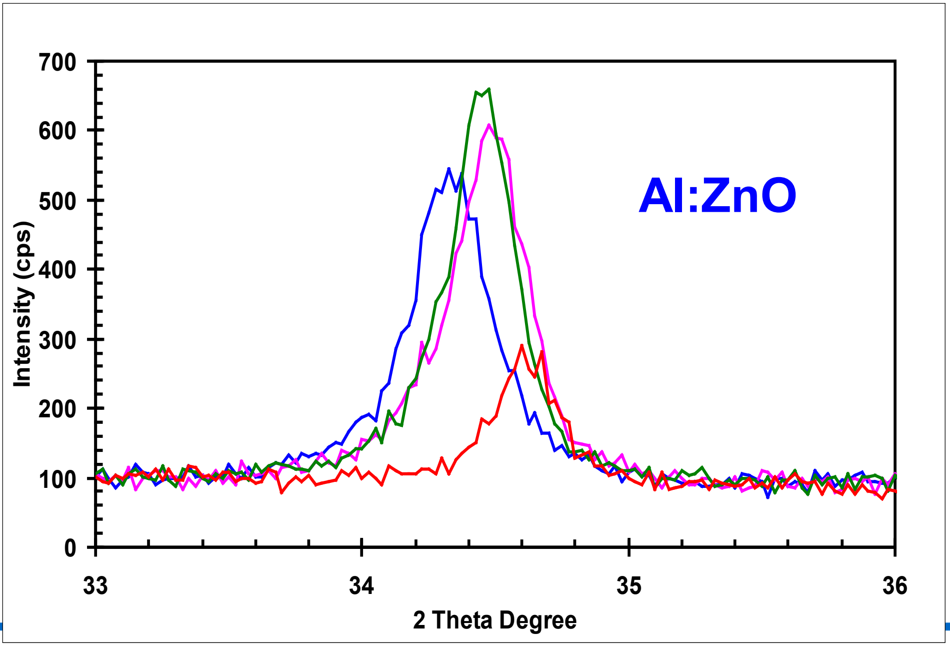


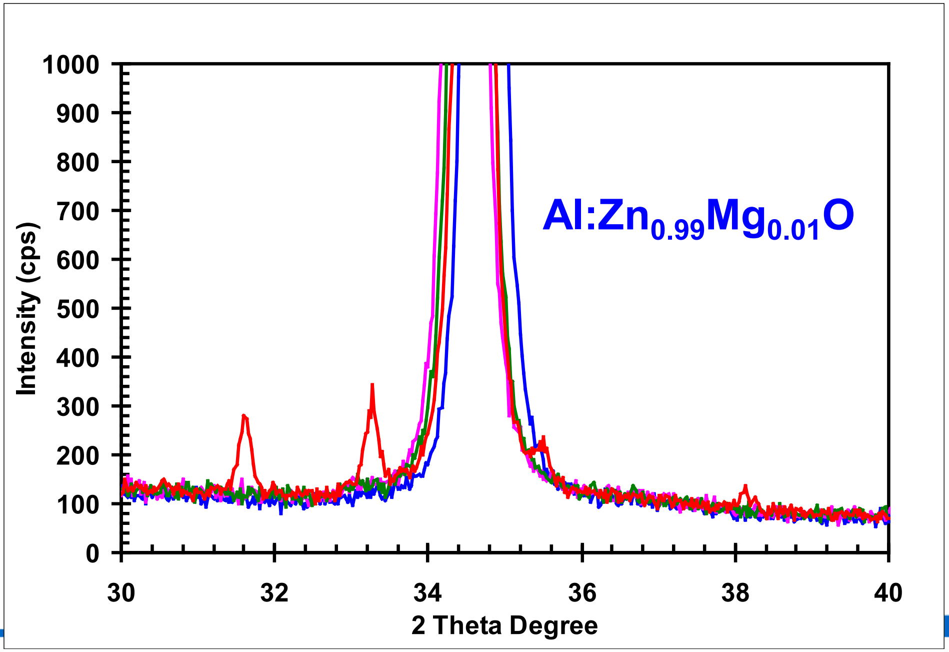
i-/Al:ZnO 0.2 μm => ~2 μm, porous, two layers

Structural Degradation of ZnO in DH

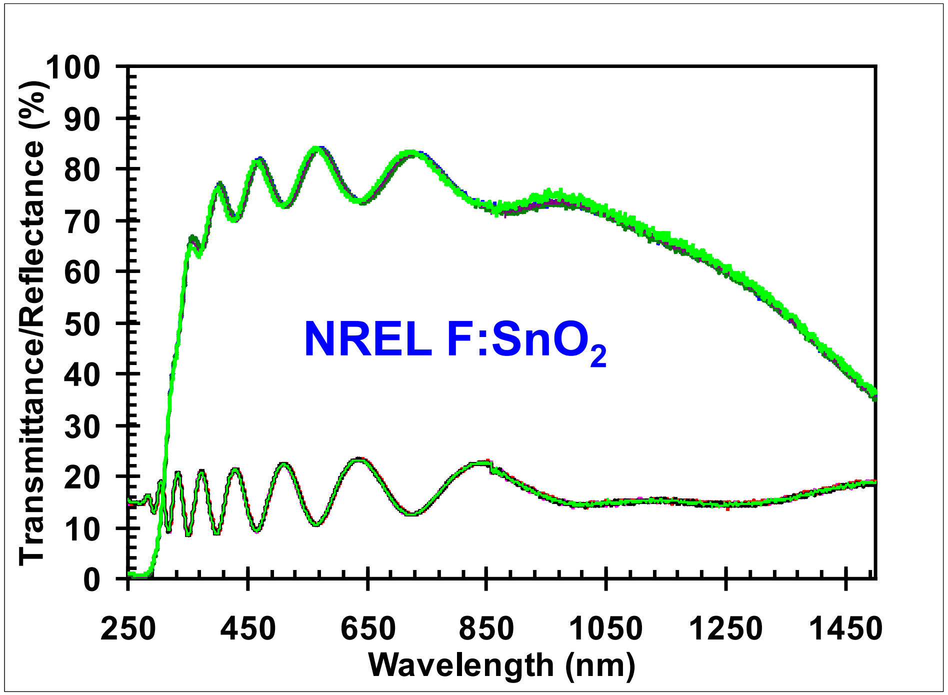


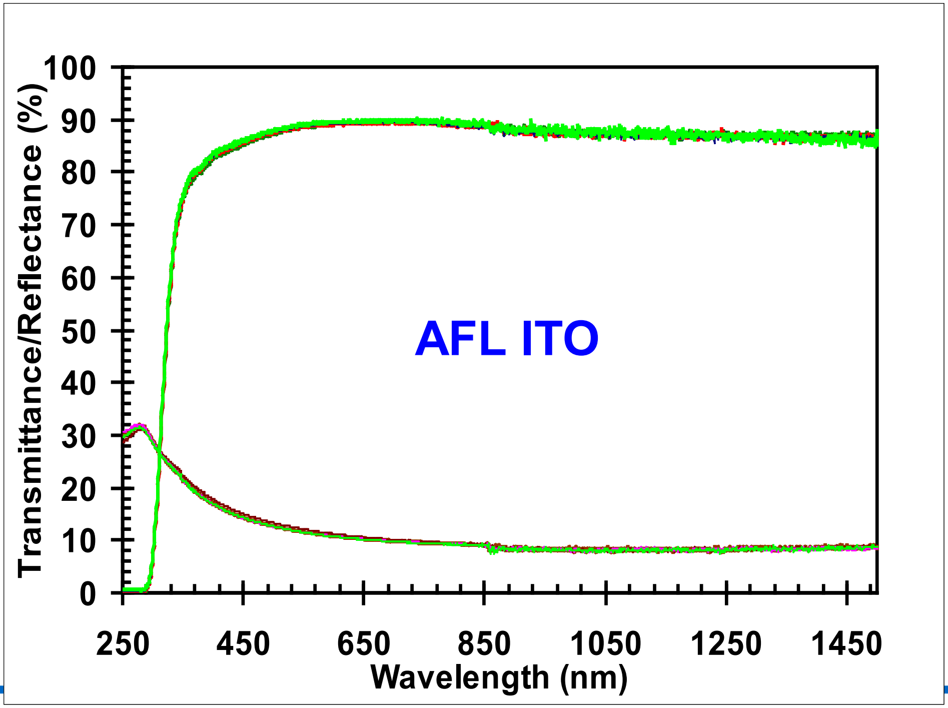


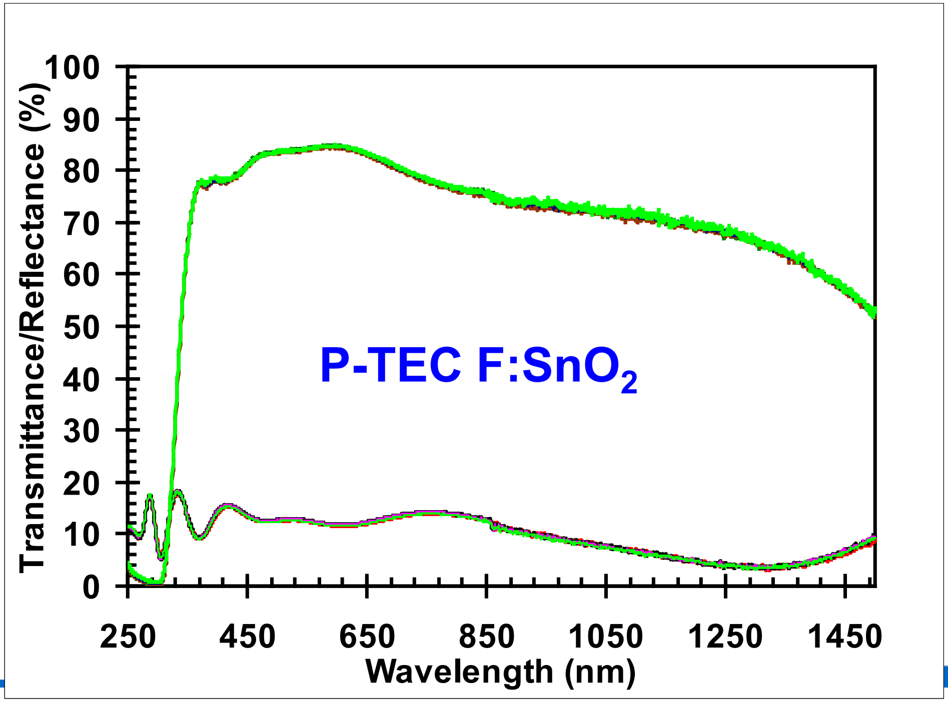




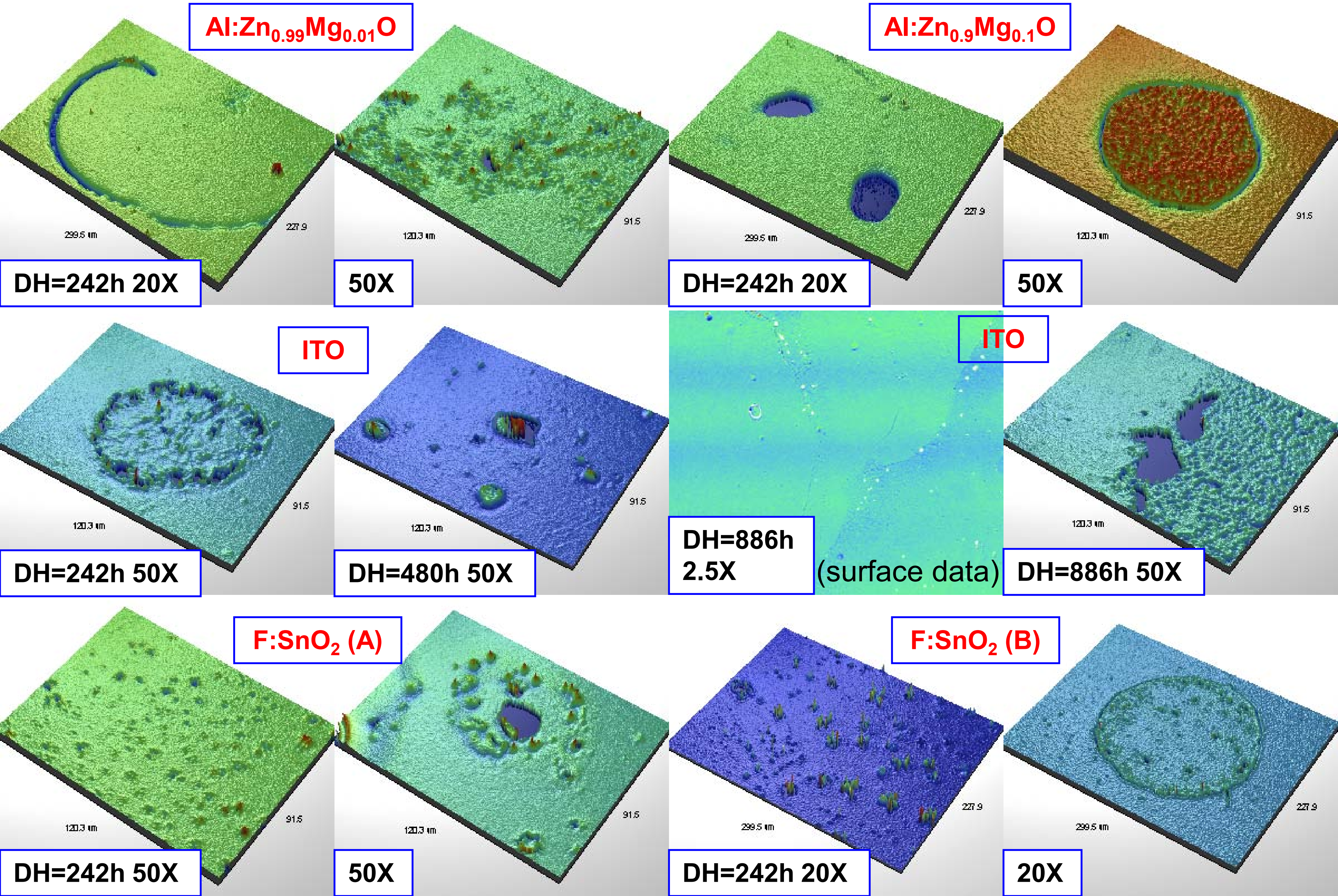
"Apparent" Optical Stability of ITO & $F:SnO_2$ Coatings at DH = 480 h







More Morphological Degradations



Electrical Degradation

Degradation Rate:

ZnO >> ITO > F:SnO_2

For Al-doped ZnO:

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

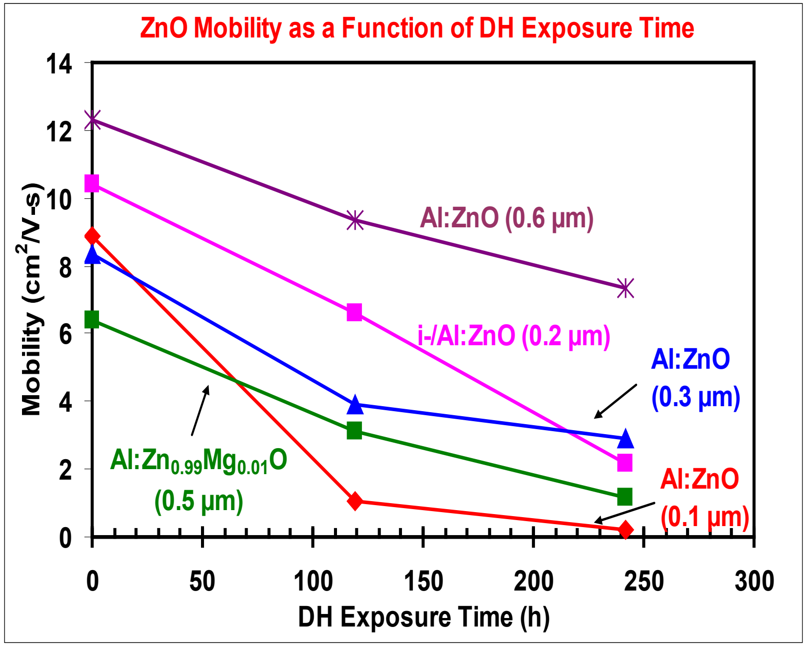


Table 1. Sample Data and Sheet Resistance Changes upon Damp Heat Exposure

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} (^oC)	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

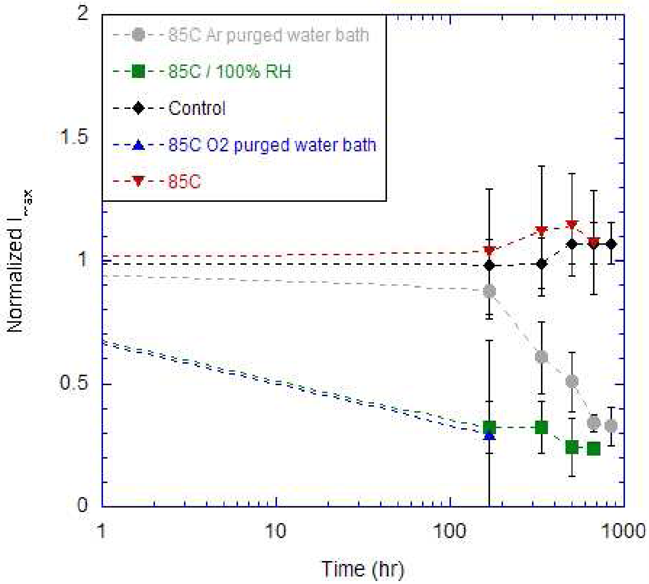
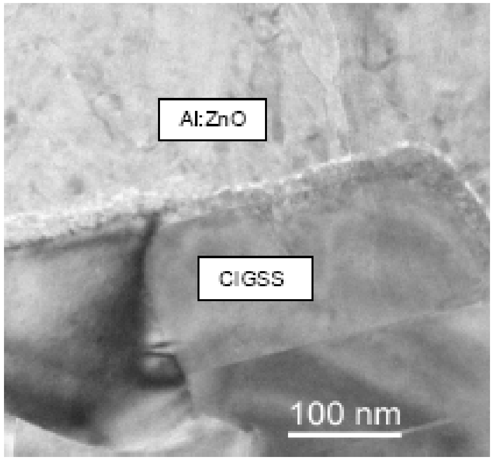


Fig. 2 Normalized I_{max} from SSI cells exposed to various environments.



TEM cross-section of as-received SSI cell.

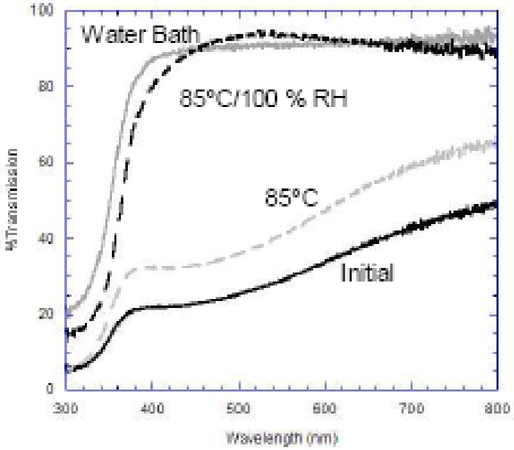


Fig. 6 UV/Vis of Al:ZnO samples initially and after 24 hr exposure to 85°C, 85°C/100% RH, and a water bath.

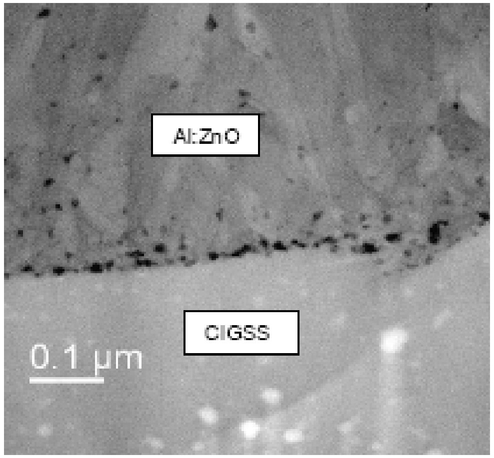


Fig. 5 TEM cross-section of SSI cell after exposure t
85°C water bath

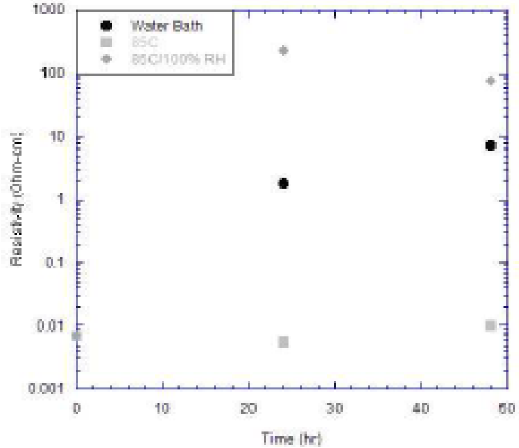


Fig. 7 Resistivity of Al:ZnO films after exposure to 85°C, 85°C/100% RH, and a water bath.

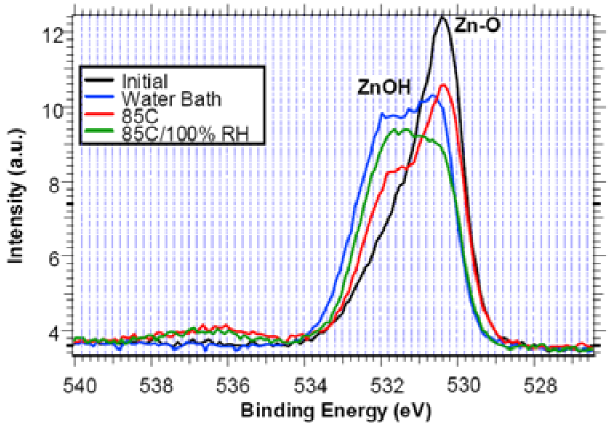


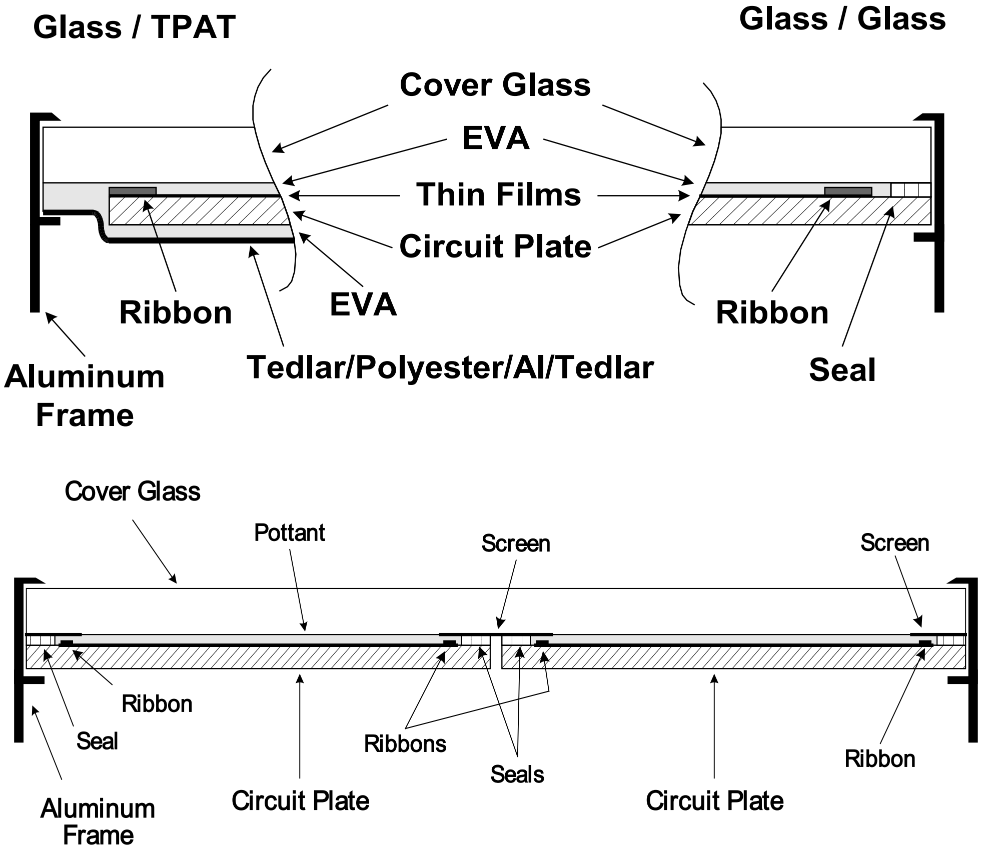
Fig. 8 XPS oxygen spectra of the sample surfaces.

National Renewable Energy Laboratory

Impact on Thin-Film PV Encapsulation and Construction

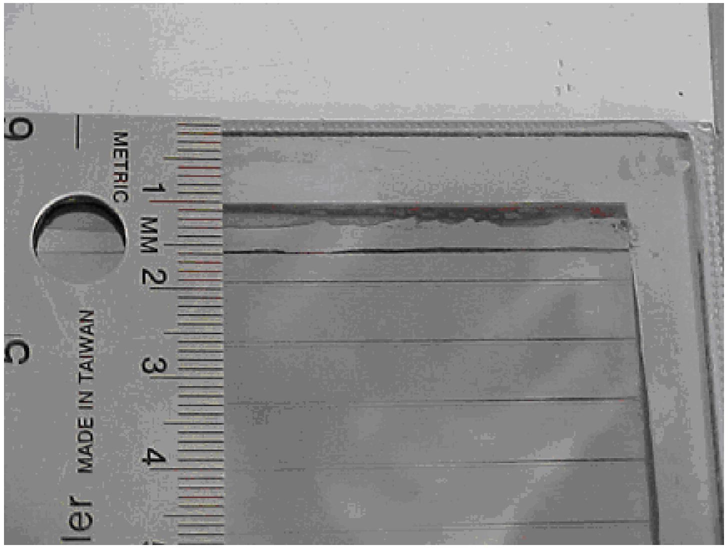
- More stringent requirements than c-Si PV
- Thin-film PV modules are mostly limited to glass/glass construction; some, e.g., CdTe and CIGS, with desiccant edge sealant to help block moisture ingress.
- Only a few flexible thin film modules (e.g., Uni-Solar's a-Si with ITO) have passed the damp heat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

CIGS with desiccant edge sealant



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

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.**

Dale E. Tarrant, PVMaT QR, 8/2004

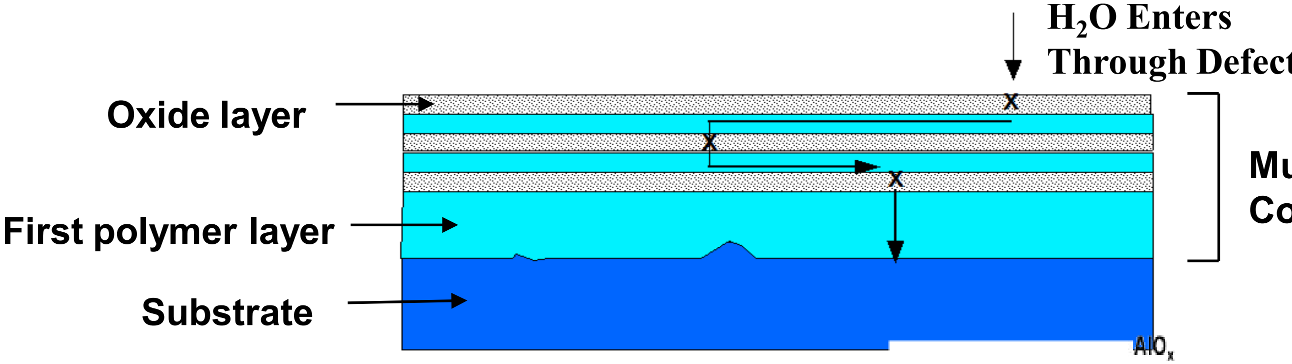
Solutions Being Investigated

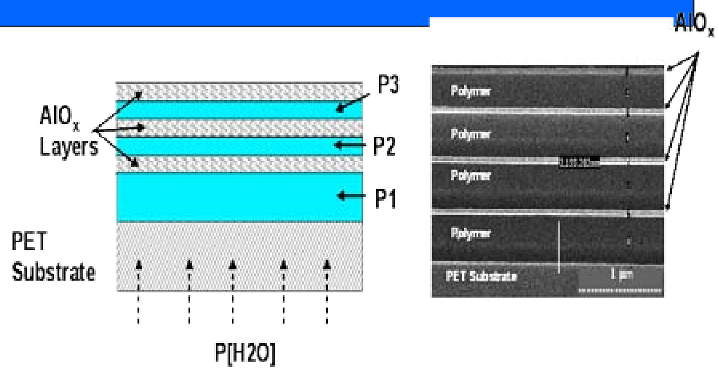
CIGS, a-Si, and OPV (rigid/flexible package)

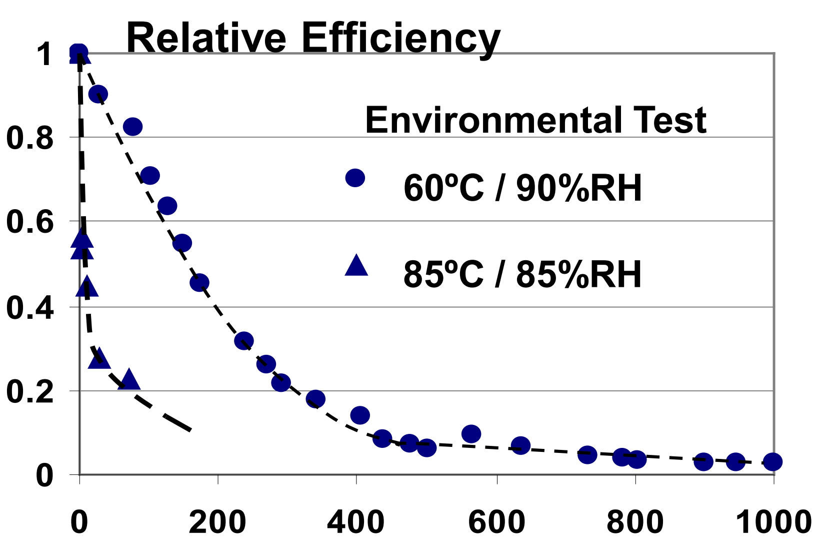
- **Use ITO to replace Al-doped ZnO**
- **more DH-stable TCOs - InZnO, InGaZnO (NREL)**
- **Mitigation ZnO with Barrier Coating**
  - -- Multilayer polymer/Al_2O_3 (PNNL)
    - -- CIGS mini-modules passed DH 1000 h test
  - -- Chemical with/without SiOxNy (NREL)
  - -- Other MO protective layers (NREL)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

L. Olsen, SPIE PV, 8/2008

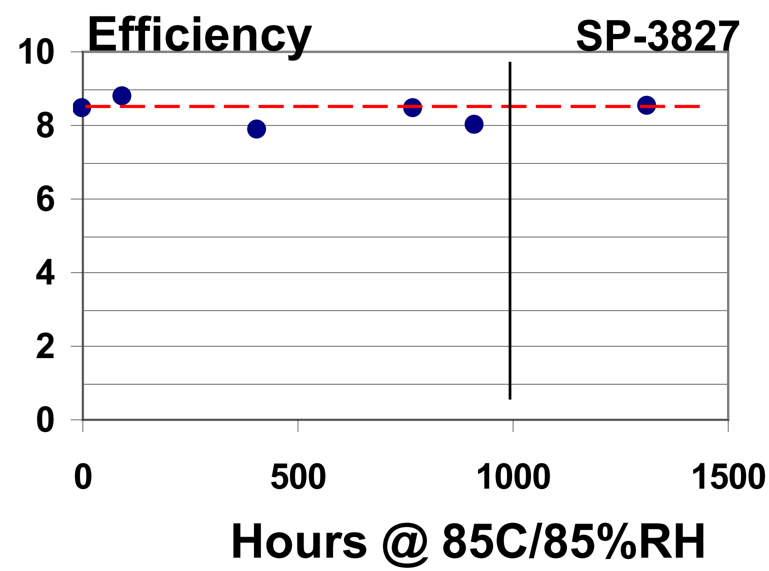
PNNL's Multilayer Moisture Barrier







Uncoated CIGS Cells with ZnO TCO's



Laminated SoloPower mini-module, 25 cm², 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)

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

Solar Energy Research Facilities (SERF)

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