

Damp-Heat Induced Degradation of Transparent Conducting Oxides for Thin Film Solar Cells

**John Pern, Rommel Noufi,*
XiaoNan Li, Clay DeHart, and Bobby To**

**National Center for Photovoltaics
National Renewable Energy Laboratory
1617 Cole Blvd., Golden, CO 80401**

*** currently with SoloPower Inc.,
5981 Optical Court, San Jose, CA 95138**

33rd IEEE PVSC, 5/12/2008, San Diego, CA

NREL/PR-520-43256

Presented at the 33rd IEEE Photovoltaic Specialist Conference held May 11-16, 2008 in San Diego, California

ACKNOWLEDGEMENTS

Dave Albin – Discussions

Steve Glick – SiO_xN_y coating

Jie Zhou – XRD

Joel Pankow – XPS

**This work was supported by the U.S.
Department of Energy under the Contract
No. DE-AC36-99GO10337 with the
National Renewable Energy Laboratory**

OBJECTIVES

- **Project Long-Term:** To achieve a high long-term performance reliability for the thin-film CIGS PV modules with more stable materials, device structure designs, and moisture-resistant encapsulation materials and schemes.
- **Current work:** To evaluate the DH stability of various transparent conducting oxides (TCOs)
 - To identify the degradation mechanisms & quantify degradation rates.
 - To seek chemical and/or physical mitigation methods, and explore new materials.
 - **Important Note:** Direct exposure to DH represents an extreme condition that a well-encapsulated thin film PV module may ever experience.

EXPERIMENTAL

Materials:

1. ZnO sputtered on 7059 glass plates:

Semicore:

- Single layer **intrinsic ZnO (IZO)**, $\sim 0.1 \mu\text{m}$
- Single layer **Al:ZnO (AZO)**, $\sim 0.1 \mu\text{m}$, 2% Al
- Bi-layer **i-/Al:ZnO (BZO)**, $\sim 0.2 \mu\text{m}$ (for NREL CIGS cells)

ATC 2200-V:

- Single layer **Al:Zn_{1-x}Mg_xO (ZMO, x=0~0.1)**, $\sim 0.3\sim 0.6 \mu\text{m}$

2. ITO (1 commercial, AFL)

3. F:SnO₂ (2 commercial, P-TCO & P-TEC, and 1 NREL, L6A3)

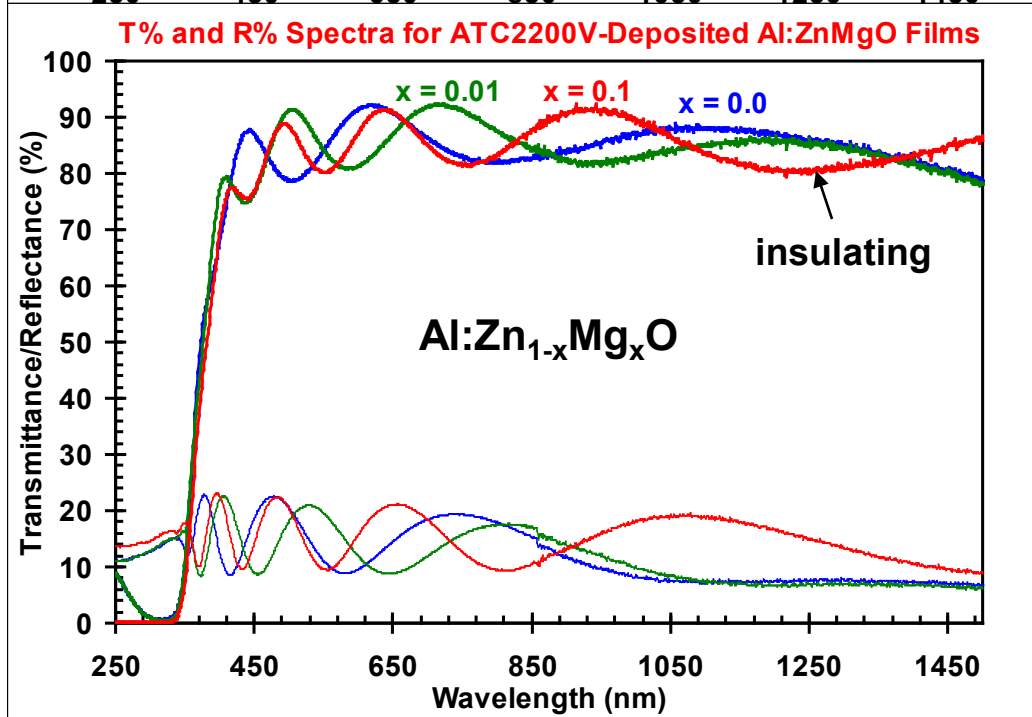
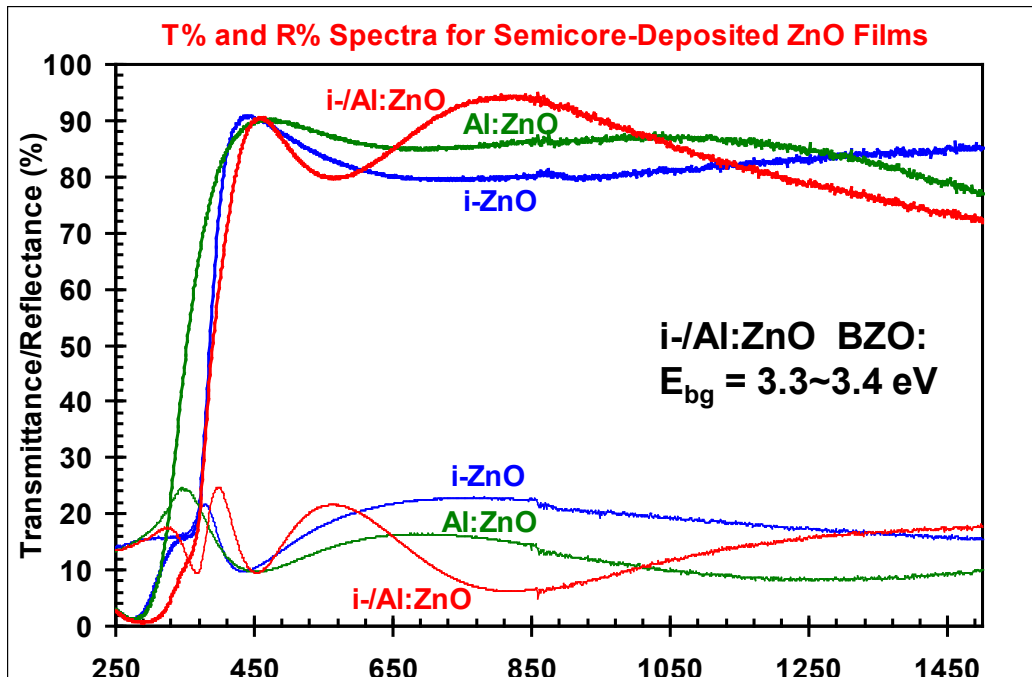
Accelerated Stress Exposures:

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

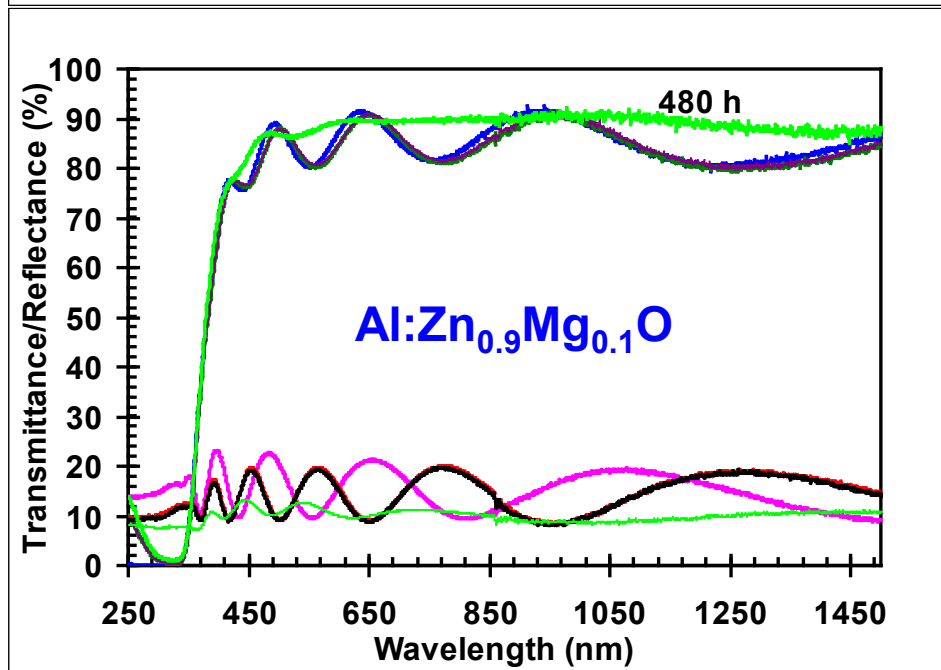
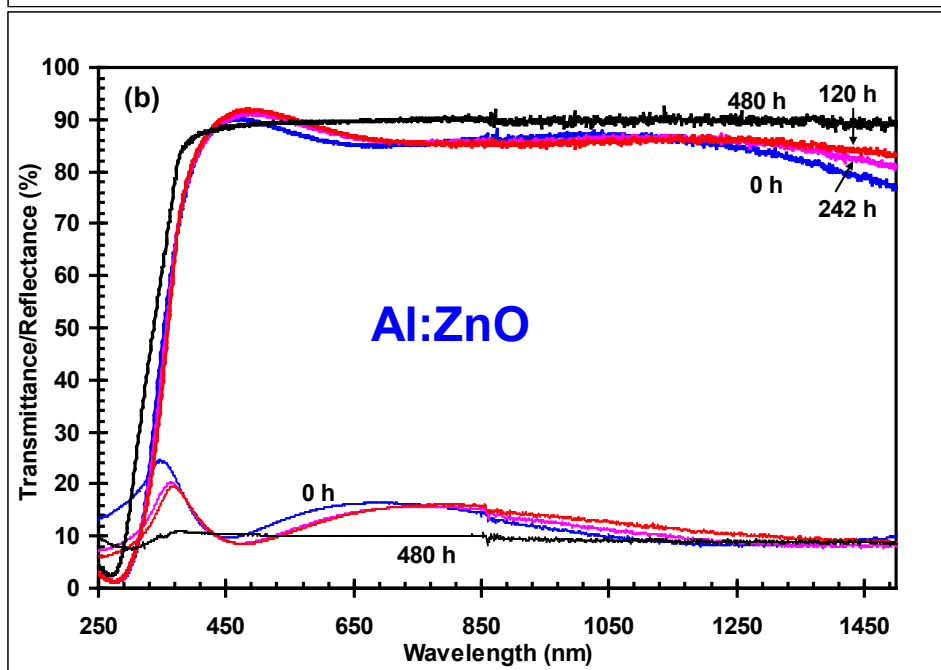
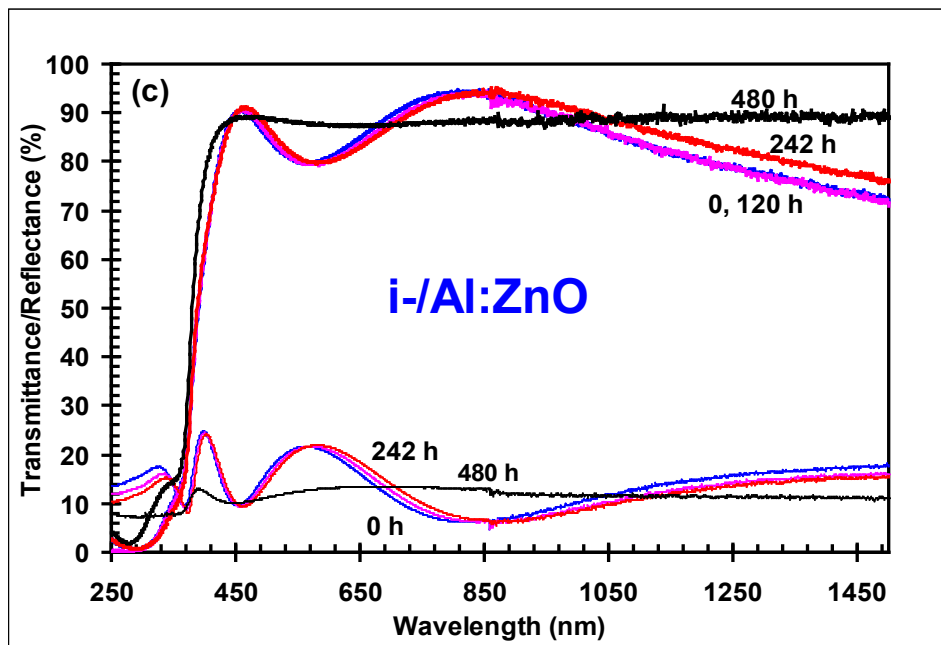
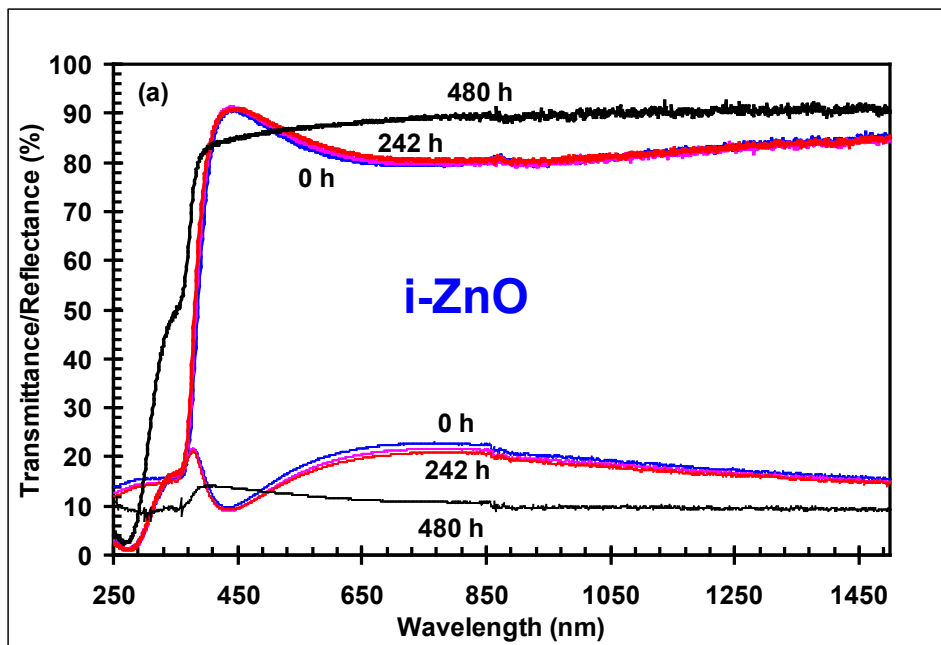
Characterization:

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

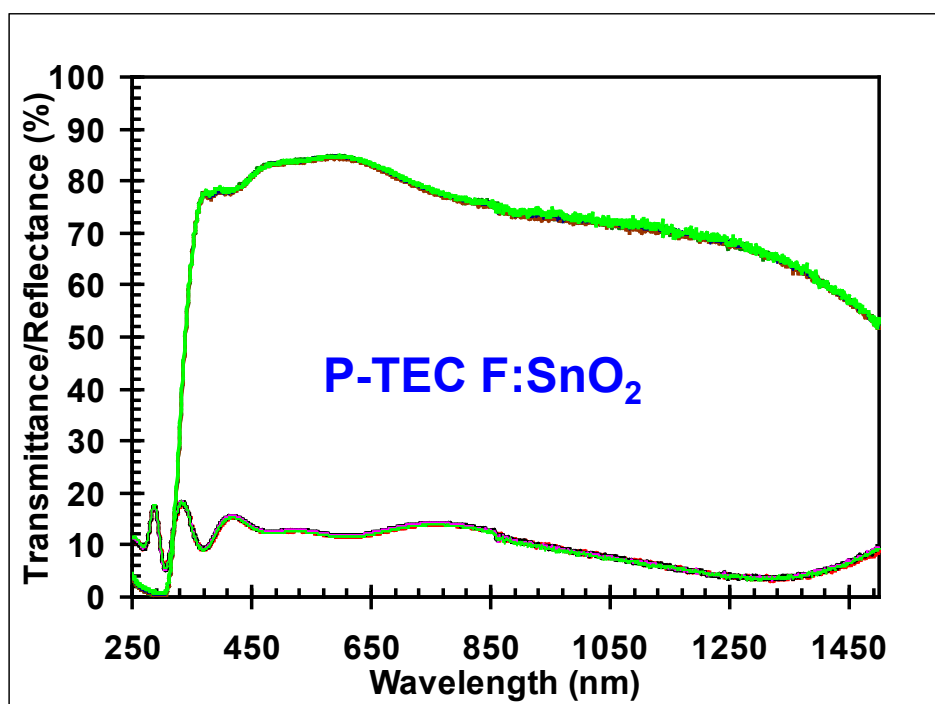
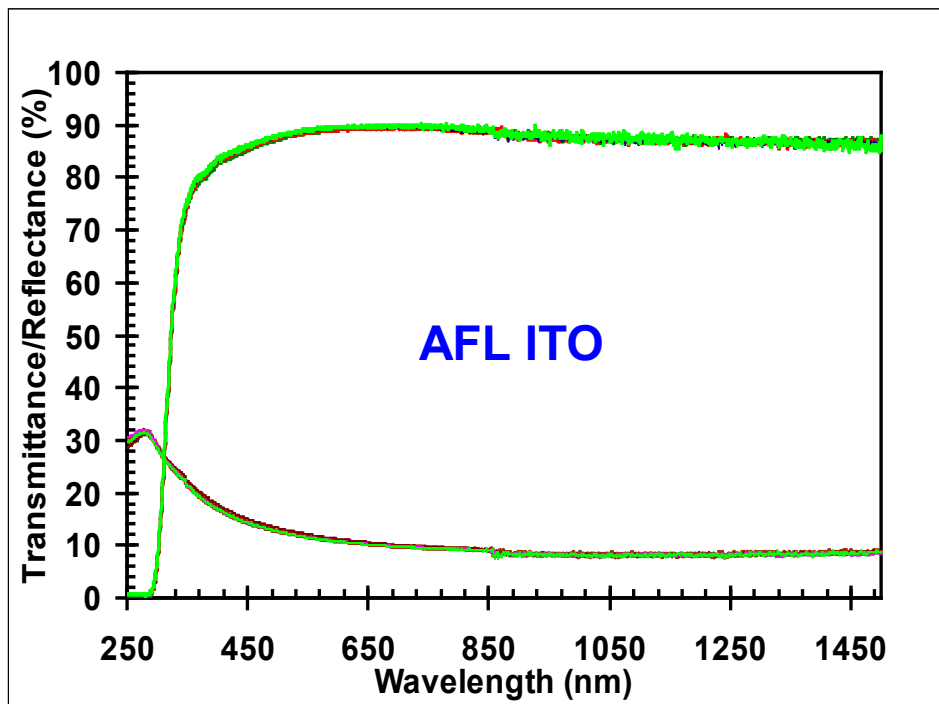
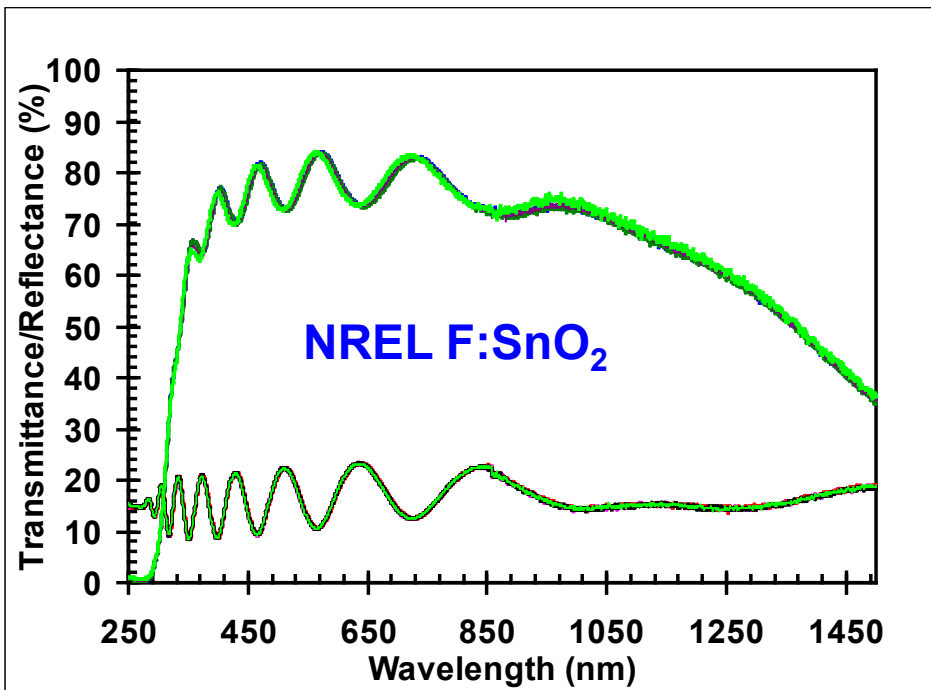
Initial T% and R% spectra of as-deposited IZO, AZO, BZO, and ZMO



Optical Degradation of ZnO in DH



Optical Stability of ITO & F:SnO₂ at DH = 480 h



Electrical Degradation

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

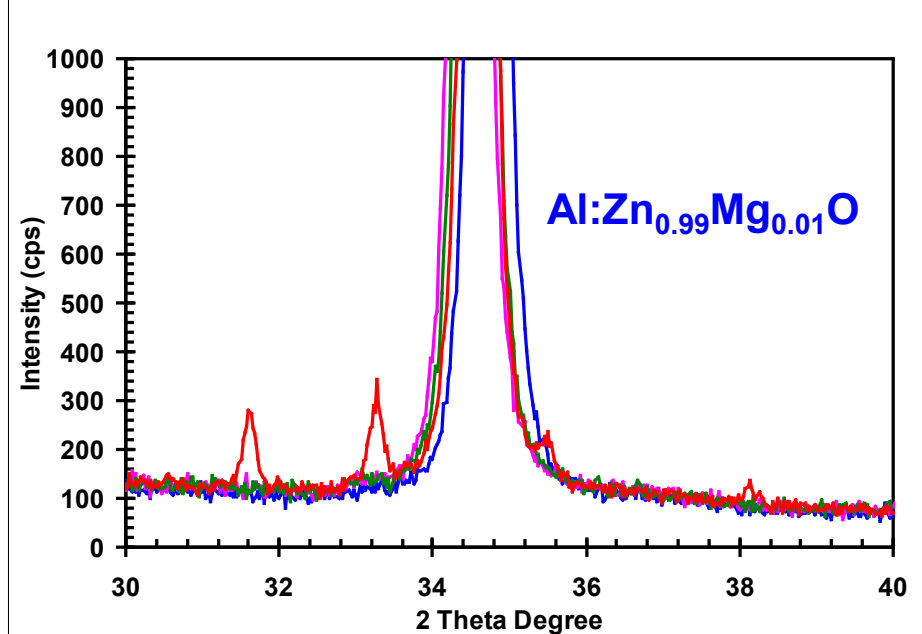
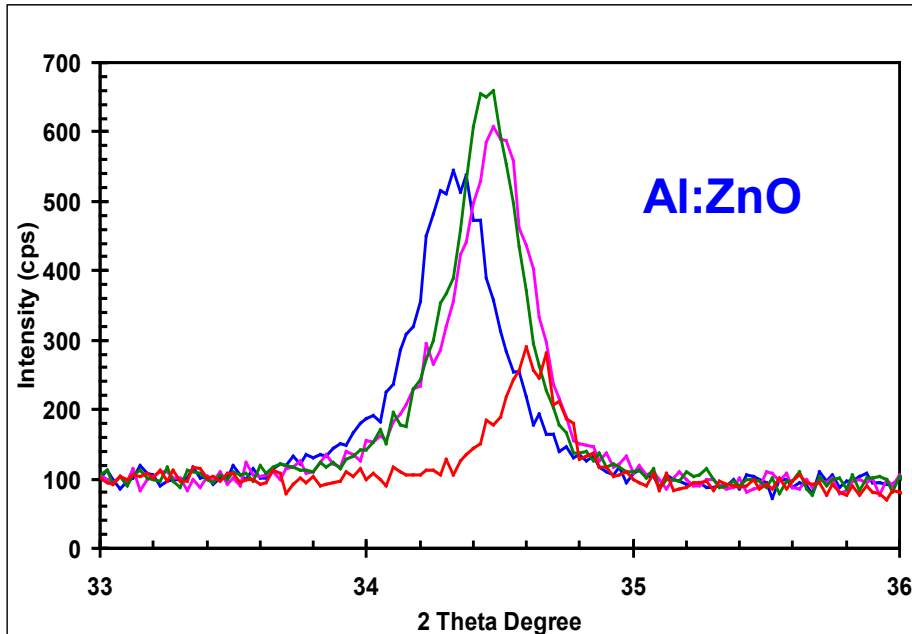
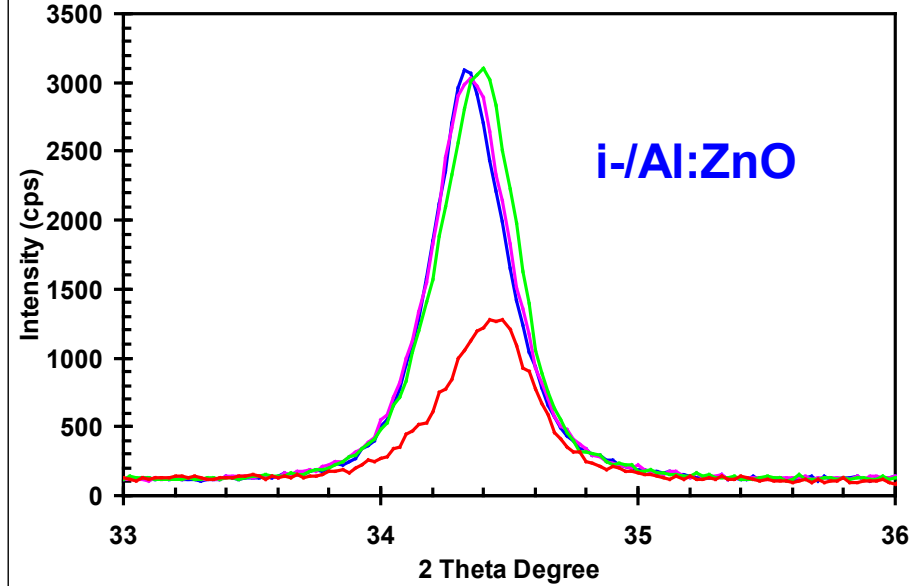
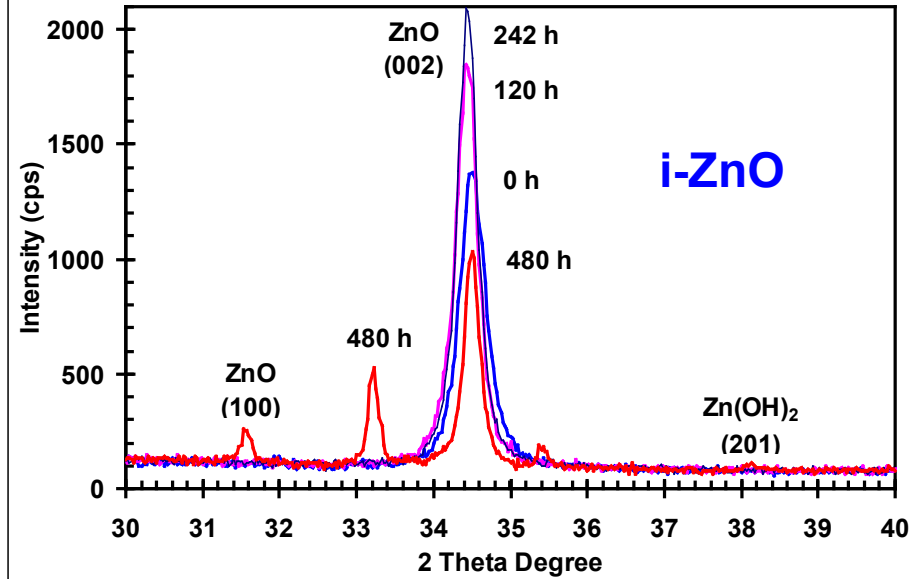
Sample ID	IZO-11	AZO-21	BZO-31	AZO-383	AZO-471	AZO-501	AZO-681	AFL-1	L6A3-1	P-TCO1	P-TEC3
Composition	int.-ZnO	Al:ZnO	i-/Al:ZnO	Al:ZnO	Al:ZnO	Al:ZnO	Al:ZnO	Sn:In ₂ O ₃	F:SnO ₂	F:SnO ₂	F:SnO ₂
MgO added	0%	0%	0%	0%	1%	10%	0%				
Dep. T _{sub} (°C)	Ambient	Ambient	Ambient	Ambient	100	100	100	N/A	N/A	N/A	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

(assumed linear degradation)

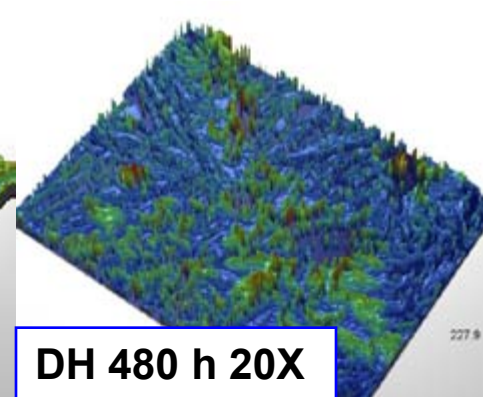
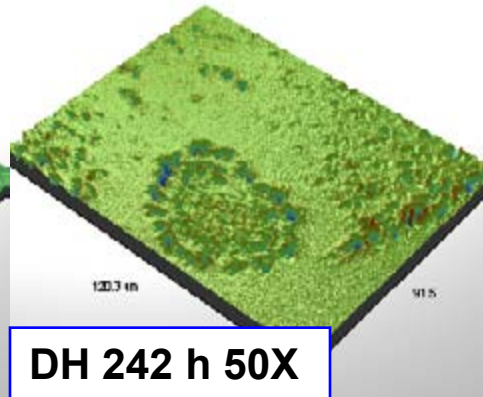
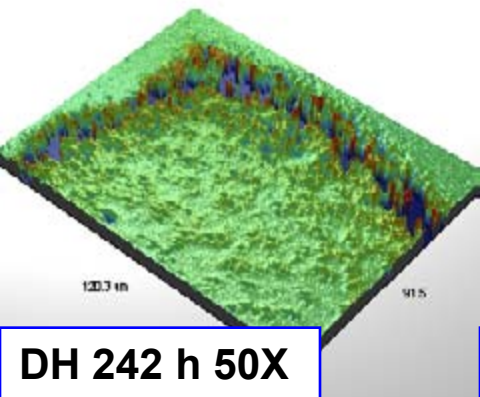
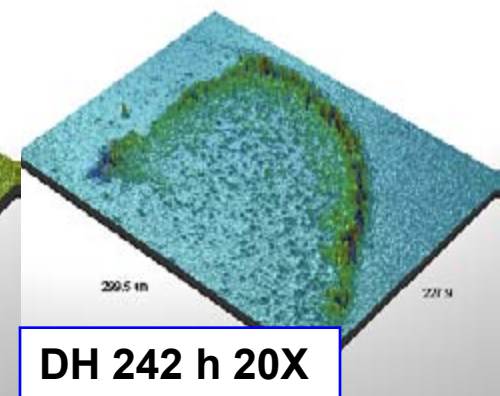
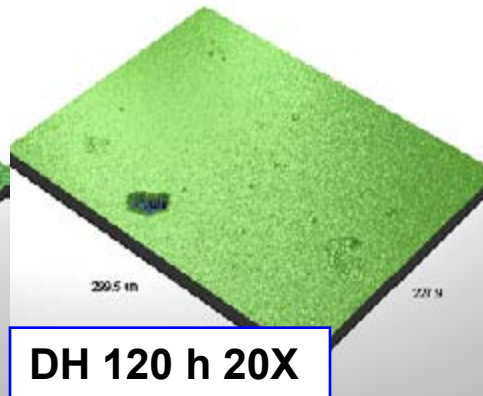
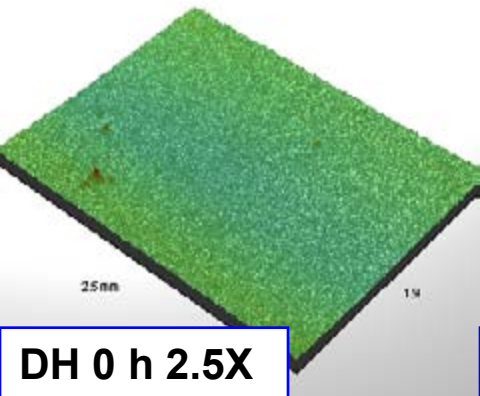
- **Degradation Rate: ZnO >> ITO > F:SnO₂**
- **For AZO:**
 - **Thickness Effect** - thicker film degraded slower
 - **Substrate Temperature Effect** - 100°C better than ambient (<60°C)
 - **“Dry-out” Effect** - “self-heal” somehow upon interval drying
 - BZO => Highly resistive at DH = 242 h if continuous exposure without interruption

Structural Degradation of ZnO in DH

XRD Peak and Pattern Changes as a Function of DH Exposure Time



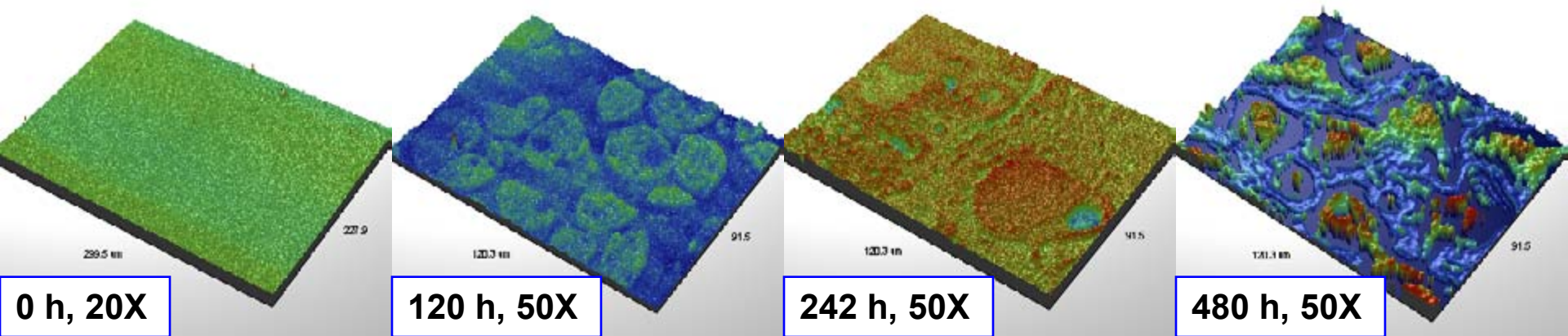
3D Images of Surface Morphology for i-ZnO upon DH Exposures (WYKO Optical Interferometer)



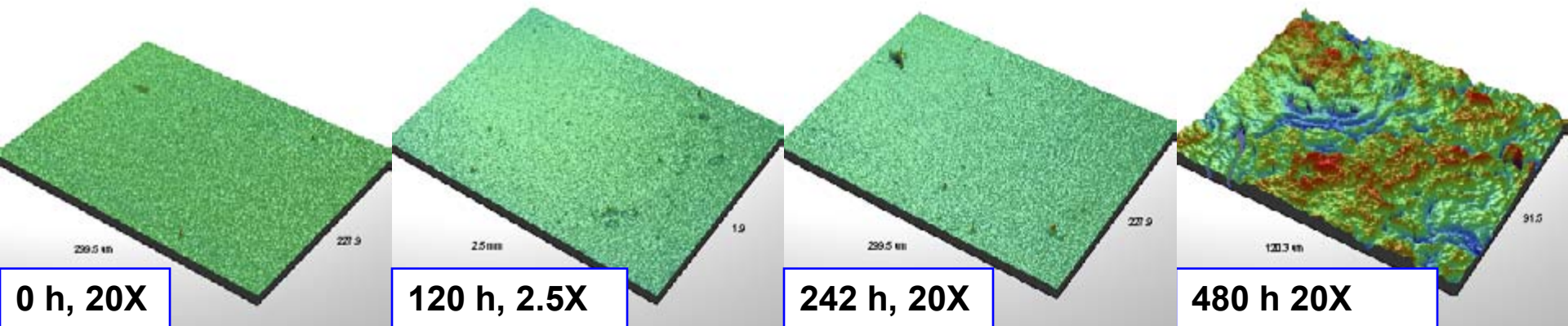
**Intrinsic ZnO,
~0.1μm**

3D Images of Surface Morphology for Al:ZnO & i-/Al:ZnO upon DH Exposures

Single-layer Al:ZnO, $\sim 0.1 \mu\text{m}$

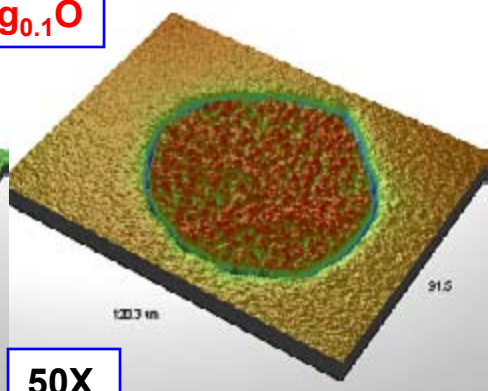
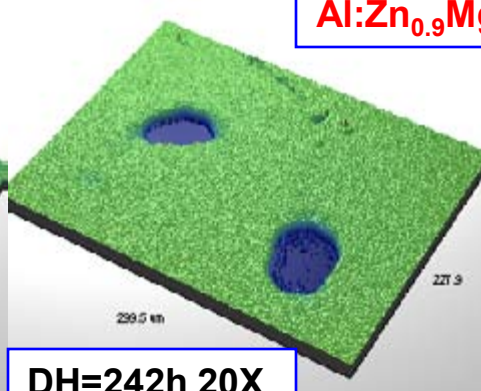
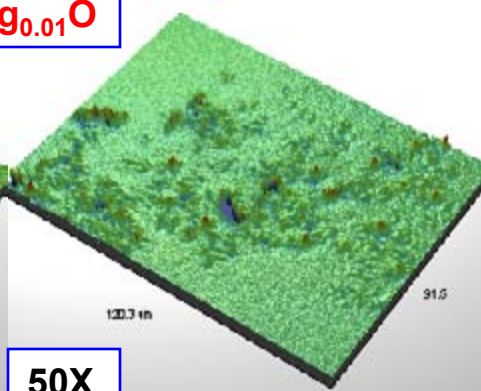


Bi-layer i-/Al:ZnO, $\sim 0.2 \mu\text{m}$



More Morphological Degradations

Al:Zn_{0.99}Mg_{0.01}O



Al:Zn_{0.9}Mg_{0.1}O

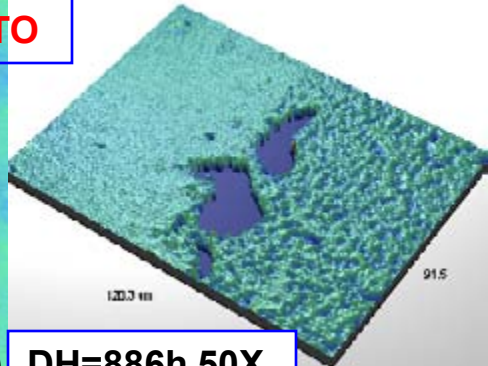
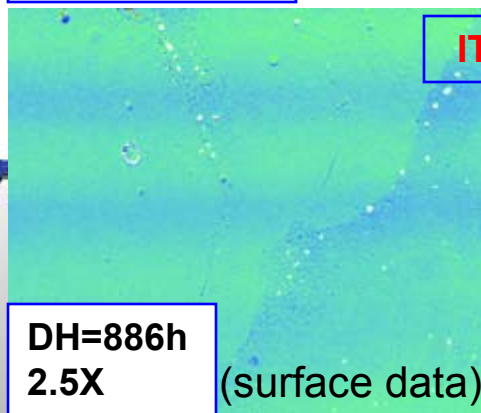
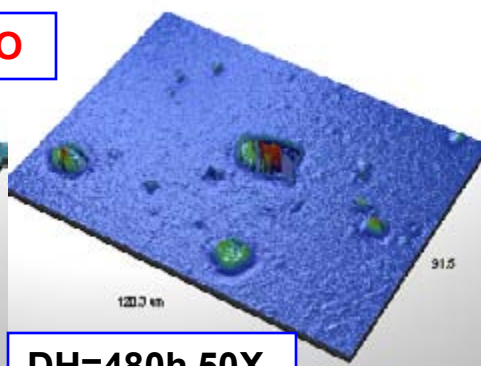
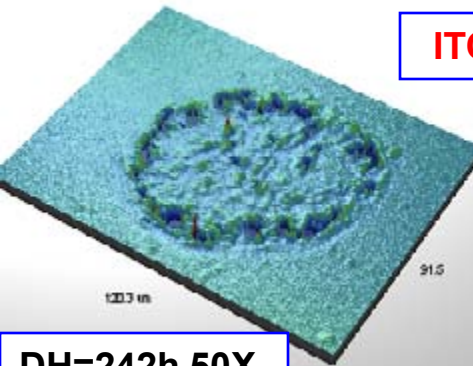
DH=242h 20X

50X

DH=242h 20X

50X

ITO



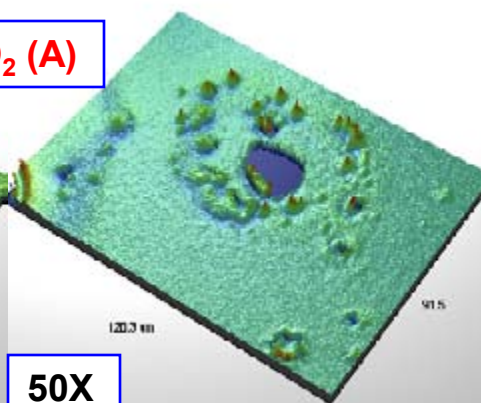
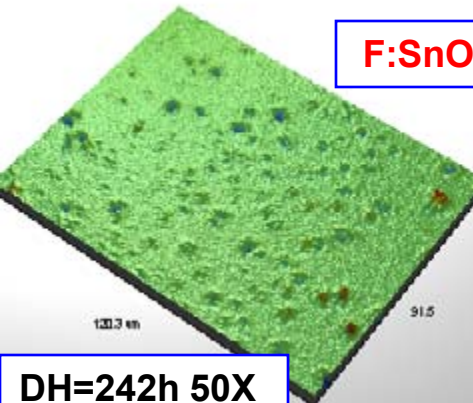
DH=242h 50X

DH=480h 50X

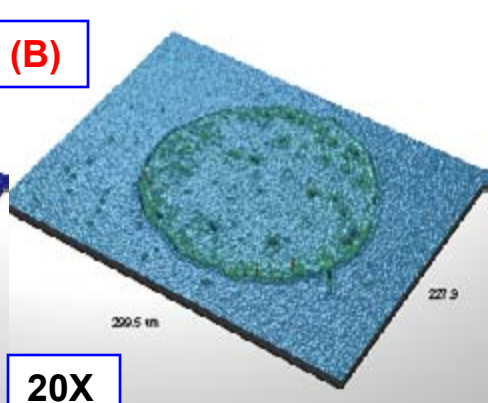
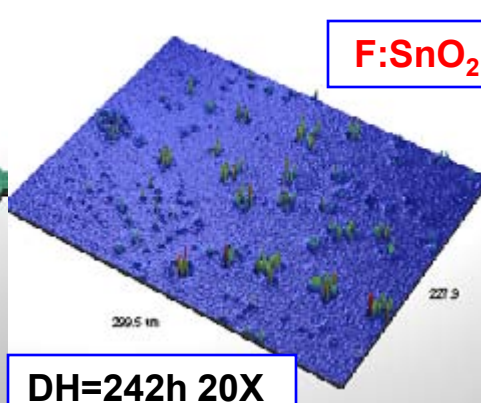
DH=886h
2.5X
(surface data)

DH=886h 50X

F:SnO₂ (A)



F:SnO₂ (B)



DH=242h 50X

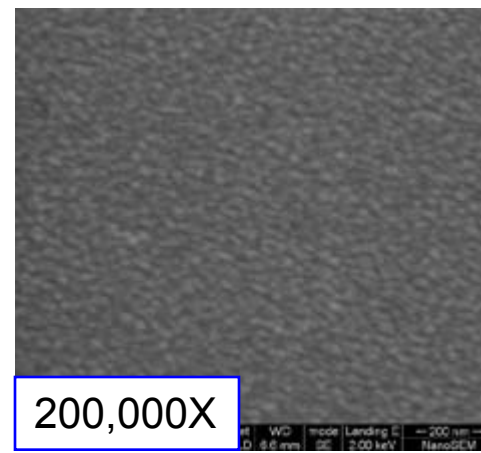
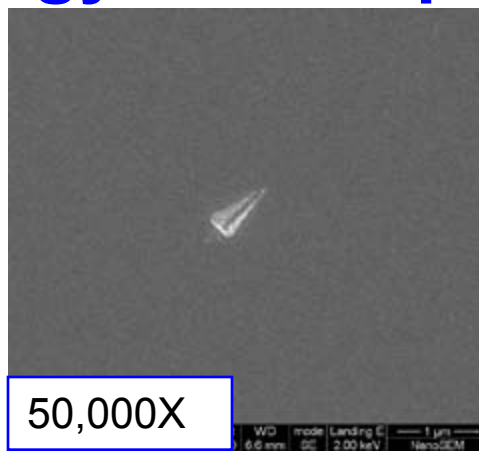
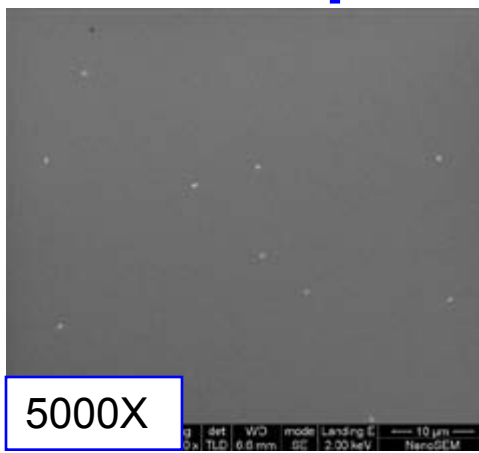
50X

DH=242h 20X

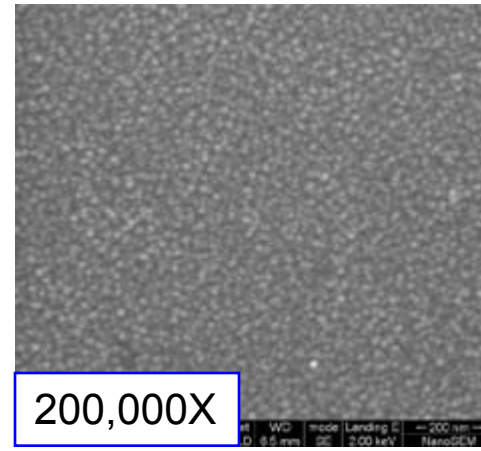
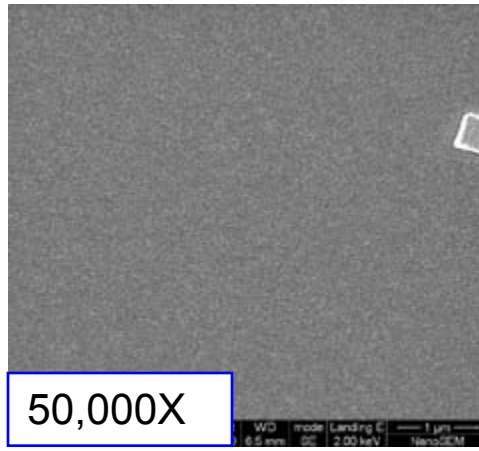
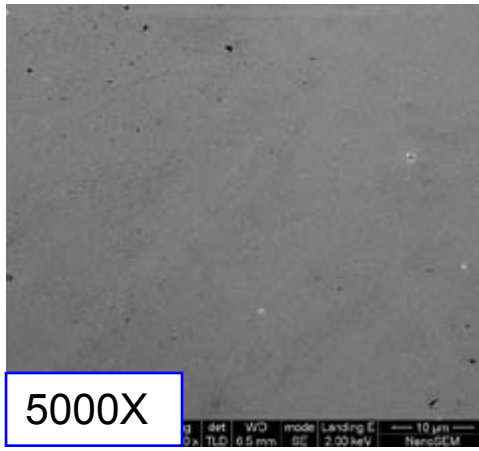
20X

SEM Surface Morphology of Unexposed ZnO Films

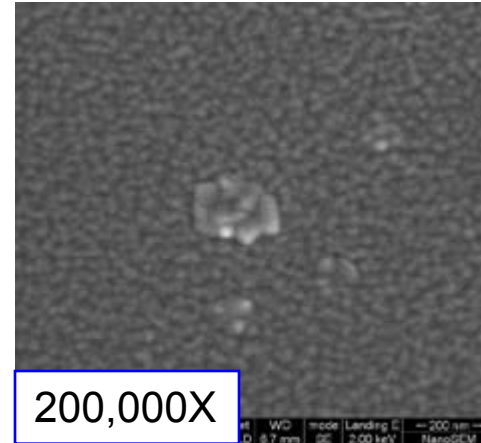
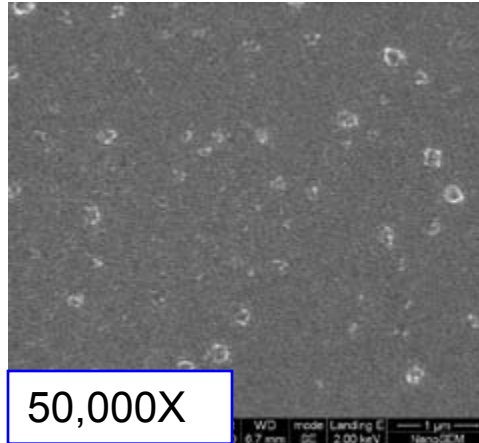
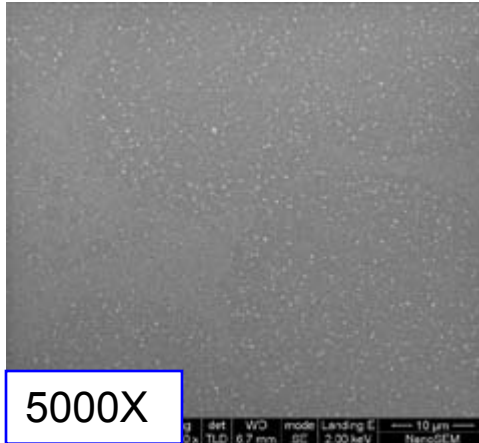
0.1 μm ,
Al:ZnO



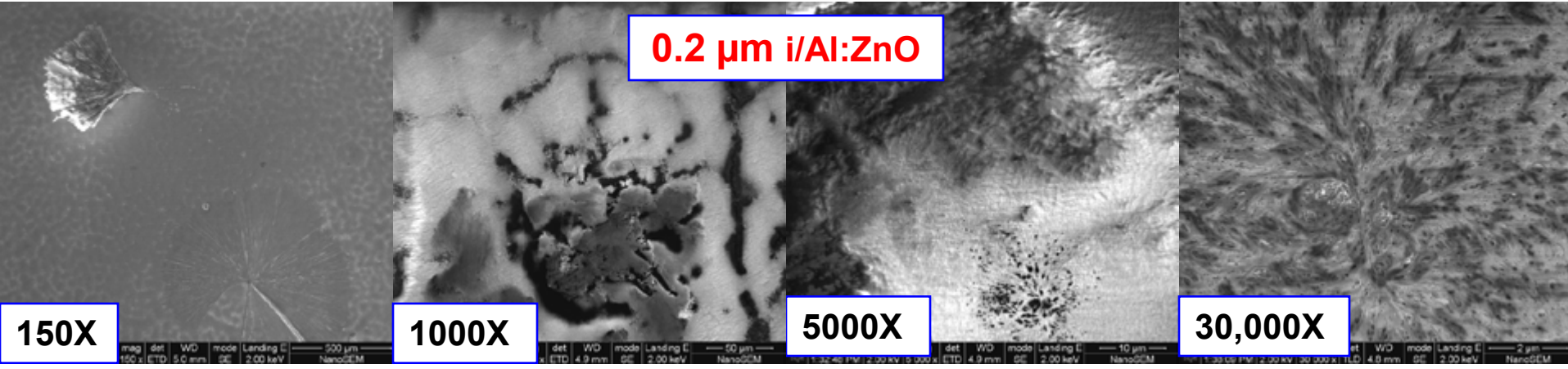
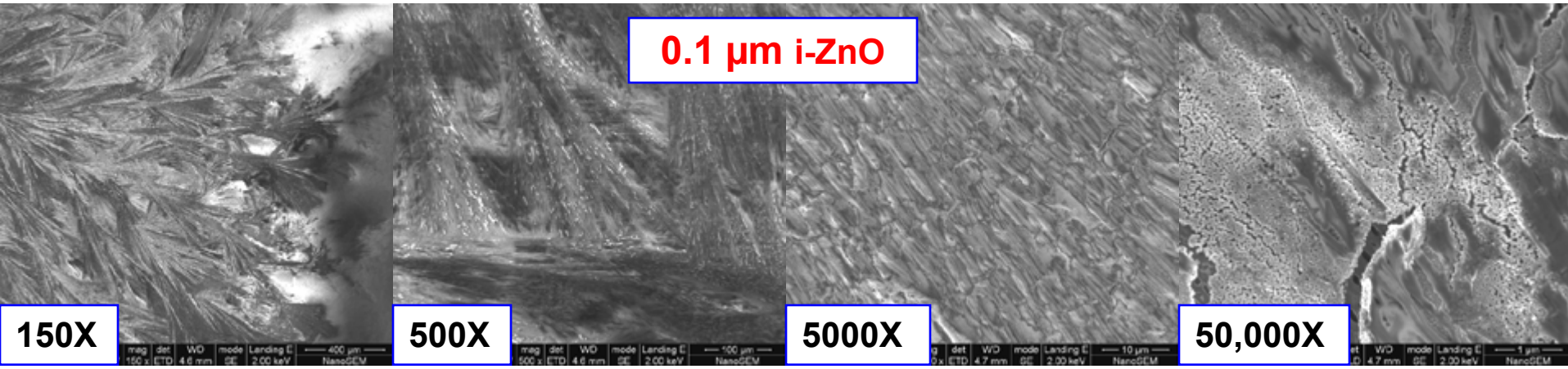
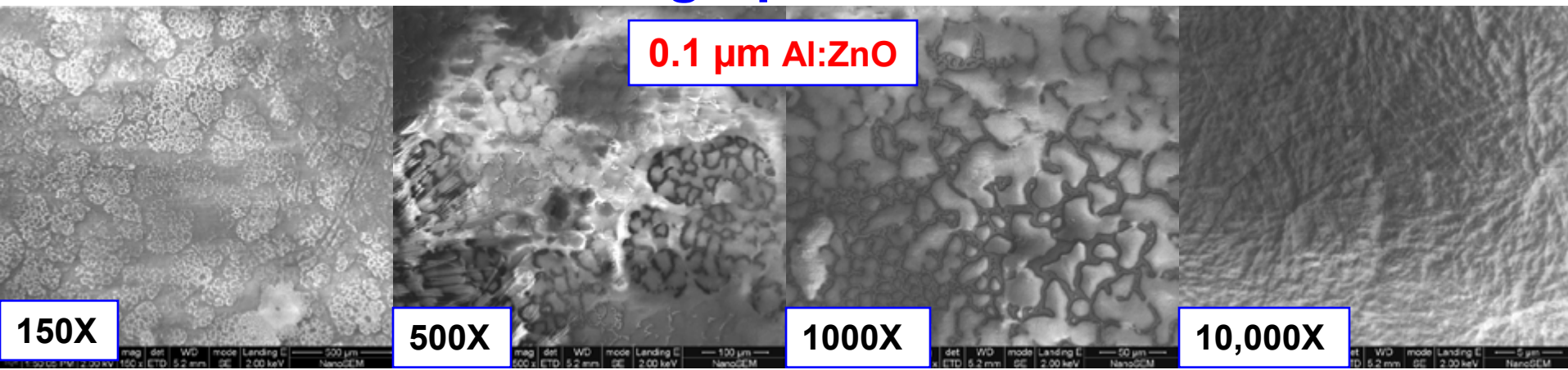
0.1 μm ,
i-ZnO



0.2 μm ,
i-/Al:ZnO



SEM Surface Micrographs for ZnO at DH=480 h

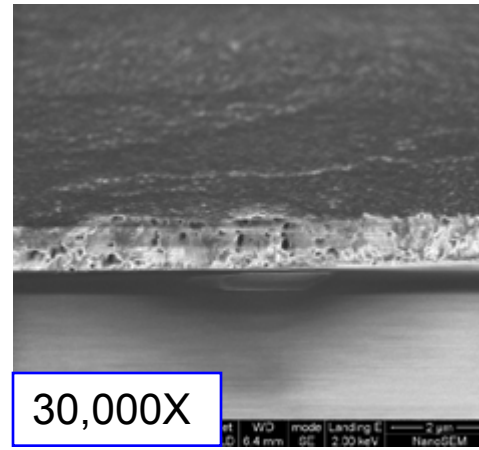
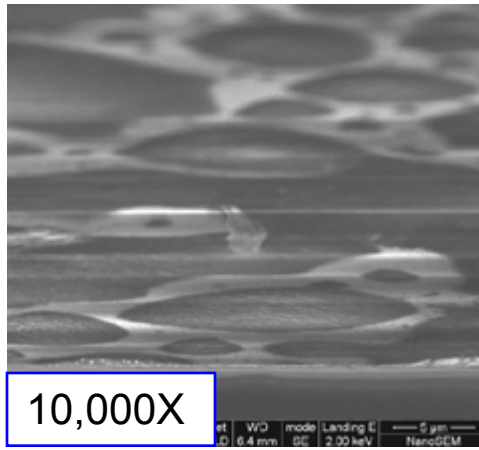


SEM (10° tilt) Cross-Section/Surface Morphology of ZnO Films

DH=480 h

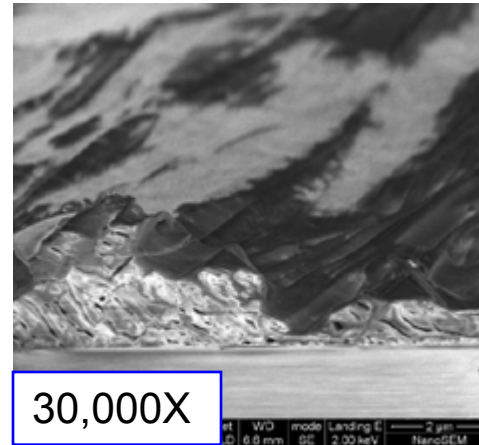
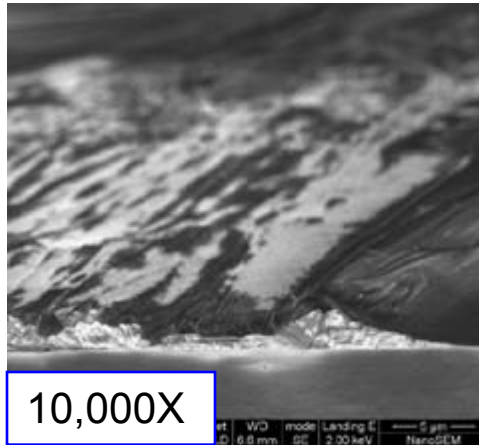
Al:ZnO

0.1 μm =>



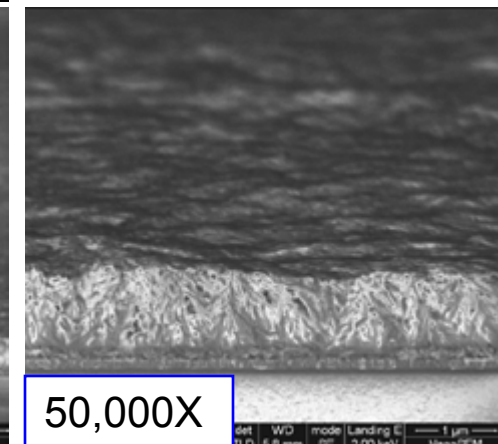
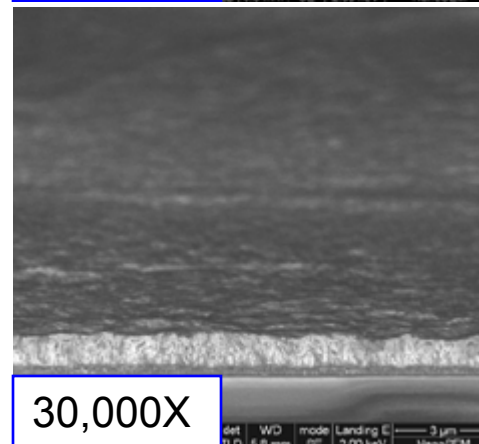
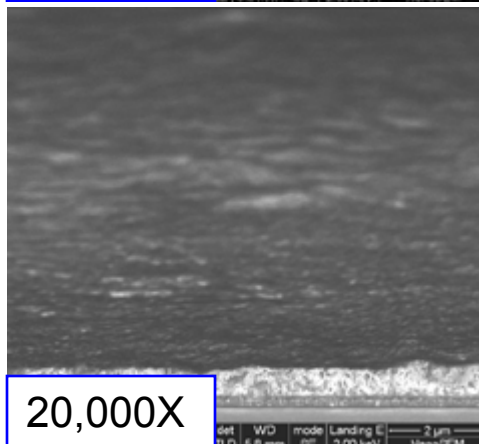
i-ZnO

0.1 μm =>



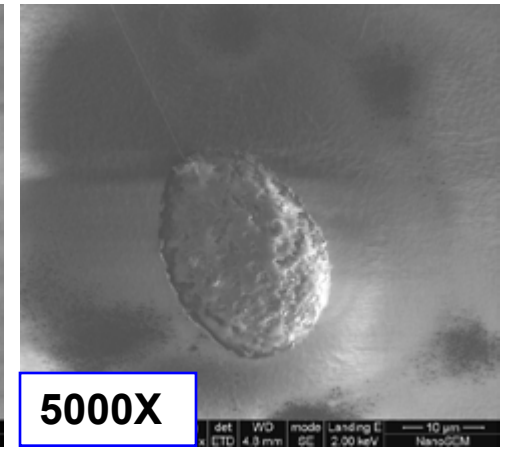
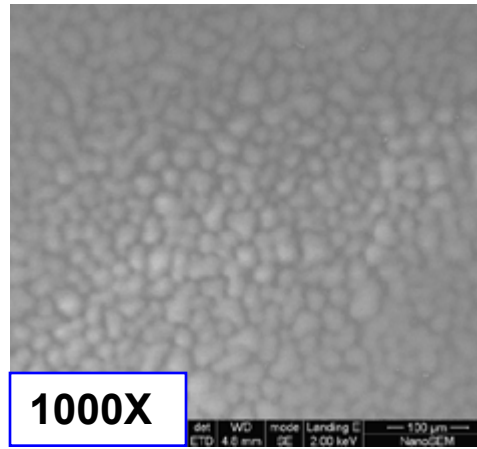
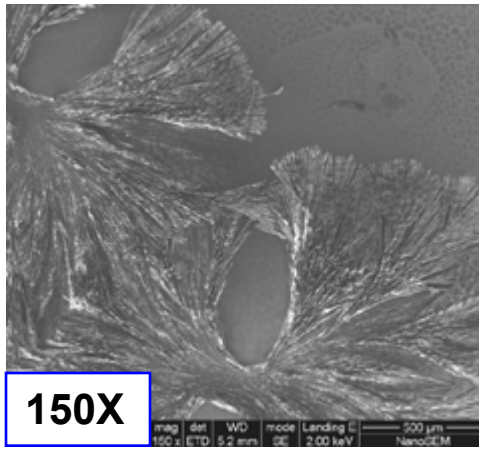
i-/Al:ZnO

0.2 μm =>

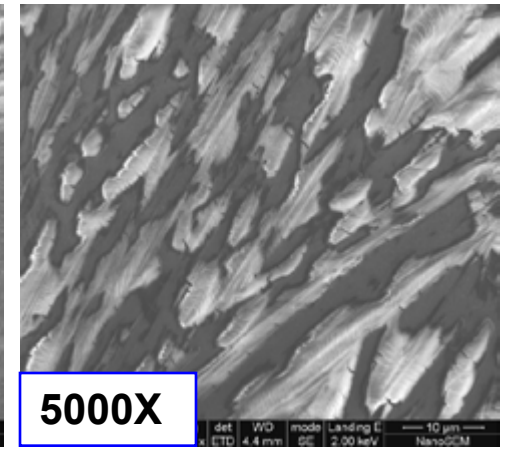
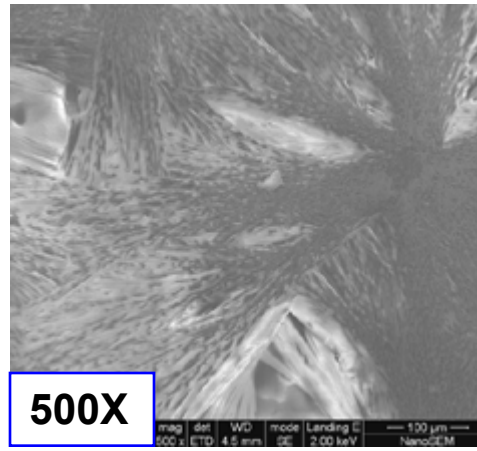
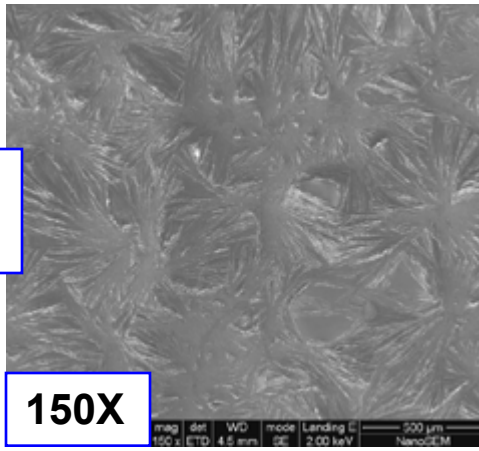


SEM Surface Micrographs for Al:ZnMgO at DH=480 h

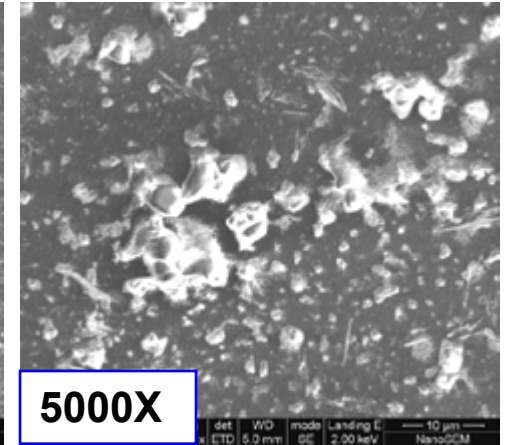
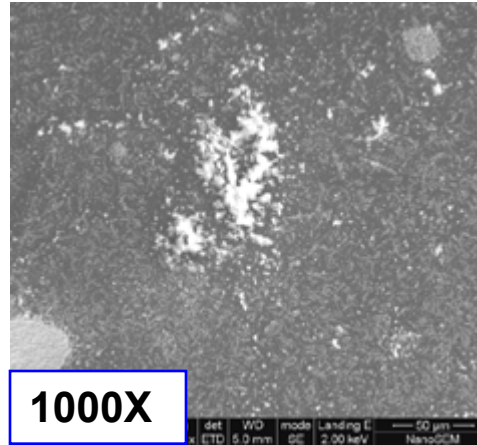
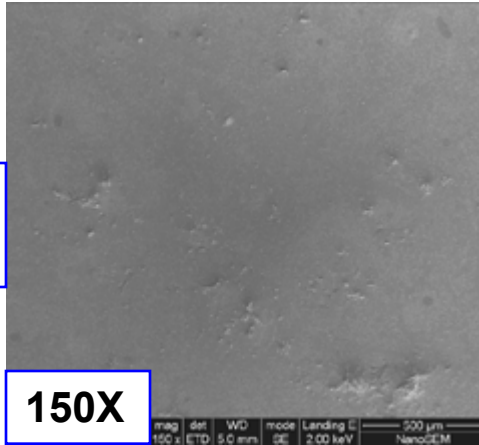
0.3 μm
Al:Zn_{1.0}Mg_{0.0}O



0.5 μm
Al:Zn_{0.99}Mg_{0.01}O

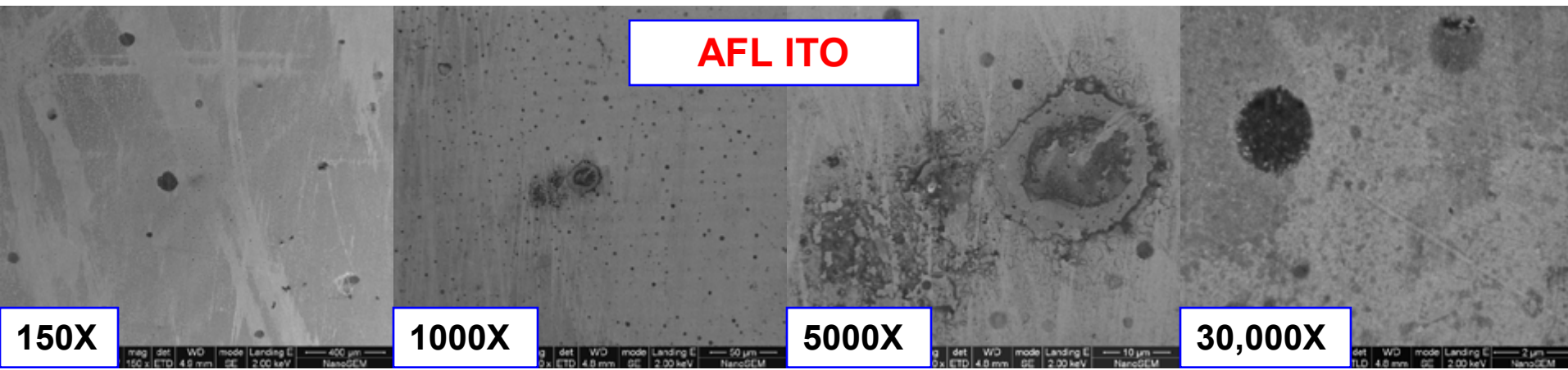


0.5 μm
Al:Zn_{0.9}Mg_{0.1}O

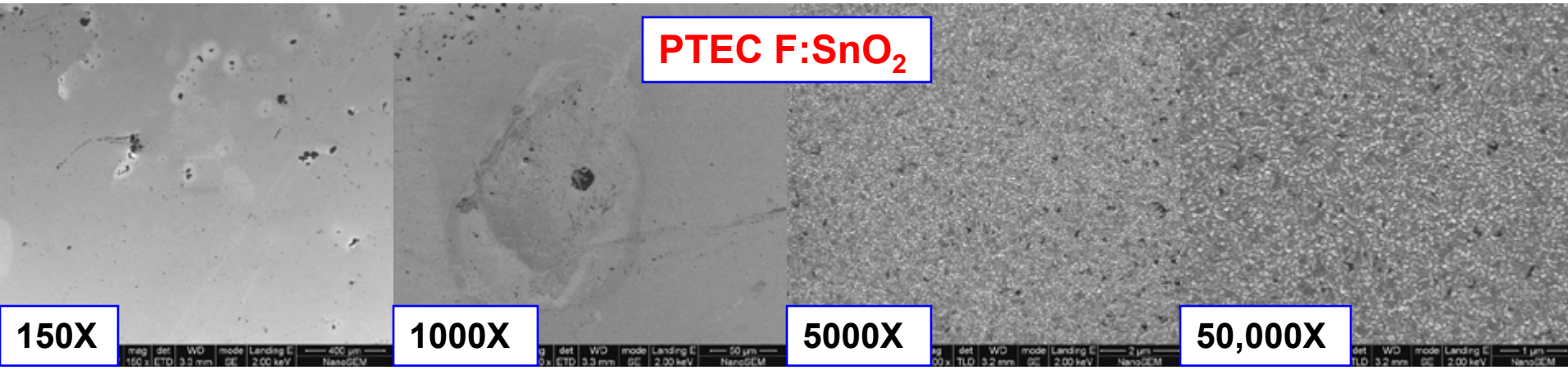


SEM Surface Micrographs for ITO & TCO at DH=886 h

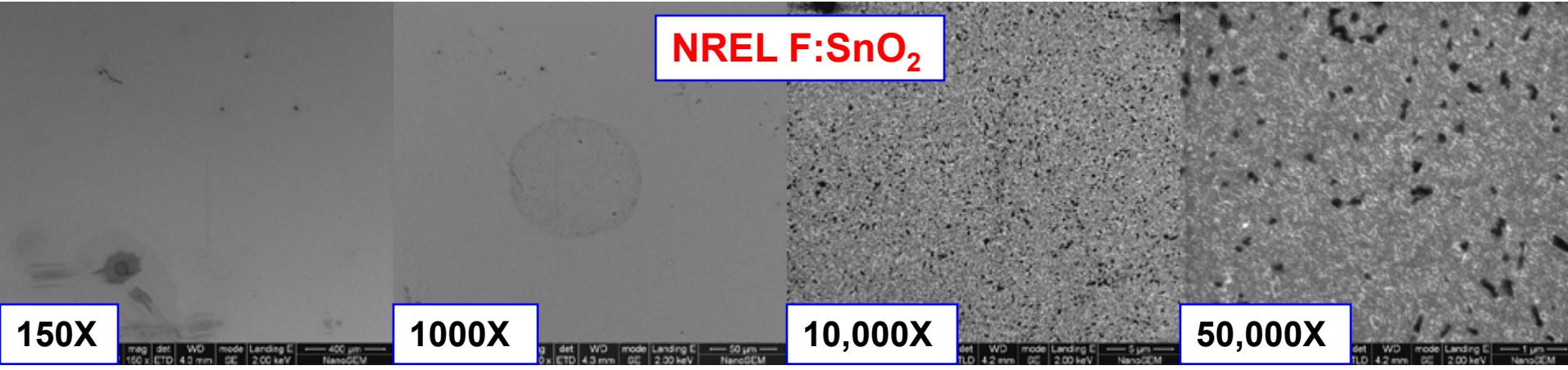
AFL ITO



PTEC F:SnO₂



NREL F:SnO₂



DH-Induced Degradation Mechanisms

The temporal process of DH-induced degradation is proposed to involve

1. first hydrolysis of the oxides at some sporadic “weak” spots,
2. swelling and popping of the hydrolyzed spots due to volume increase,
3. “segregation” of hydrolyzed regions causing discontinuity of electrical path,
4. hydrolysis of the oxide-glass interface, and
5. finally formation of insulating $M(OH)_2$ (& MO) along with visible delamination over larger areas.

CONCLUSIONS

- Clear evidence of degradation in the optical, electrical, and structural properties of the ZnO, ITO, and F:SnO₂ on glass substrates upon direct damp heat exposures.

Degradation Rate in DH: ZnO >> ITO > F:SnO₂

- ZnO & ZnMgO showed rapid degradation into highly resistive films in DH.

- Thickness effect (thicker film degraded slower)
- Substrate temperature effect (100°C better than ambient)
- Dry-out effect (“self-heal” somehow upon interval drying)

- **Future Work to Investigate:**

- interconnect stability of i-/Al:ZnO on Mo
- encapsulation effects
- chemical mitigations - PDMS silane treatment
- physical mitigations - SiO_xN_y barrier oxide coating
- Experiment designs simulating actual device and module structures and encapsulation are required to better assess quantitatively the detrimental effects of the materials instability on the performance reliability of the CIGS solar cells.

Thanks for your attention!