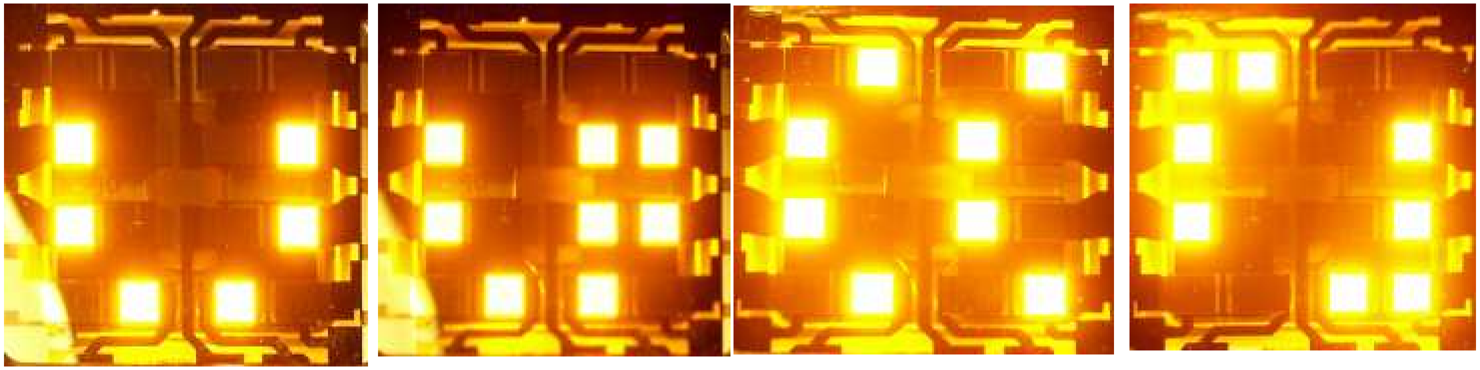

Challenges for Commercially viable Transparent Conductive Oxide Layers

Arkema Inc. 900 First Ave., King of Prussia, PA 19406
R. Y. Korotkov, L. Fang, P. Ricou, M. Bluhm, J. Coffey, C. Polsz and G. Silverman

Philips Lighting GmbH, Philipstrasse 8, Aachen, Germany 52086
M. Ruske, R, B. Krogmann and H. Schwab

Pacific Northwest National Laboratory, WA USA
A. B. Padmaperuma, and D. J. Gaspar

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Presentation Overview:

- Introduction – targets
- Homogeneity of DZO films
  - Methodology
  - Electrical properties
  - Depth profiling of the DZO
  - Optical properties
  - Roughness
- Light Out-coupling
  - Undercoat
  - Patterned glass substrate
  - High-Low-High
- OLED devices
- Conclusions

Introduction - targets

Properties	Target	ITO	TOF	ZnO:Dopant
ρ (Ω cm x10^{-4})	***2-6.0***	***2-3***	***3.5-5***	**2.0**-3
Etch Resolution (micron)	5	MN	poor	MN
Surface roughness (nm RMS)	2-10	1-5	4-20	3-6
Maximum peak to valley ($Z_{max,}$ nm)	30-40	30	>50	30-60
φ_B (eV)	4.5-5	4.7	4.9	4.3-5.1
Transmittance (%)	80-90	> 85	> 80	85-92

Advantages of doped ZnO

- Indium-free
  - Superior Economics
  - US Sustainability – not a precious metal dependent on China export policy
- High transmission
  - No blue absorption relative to Indium based TCOs

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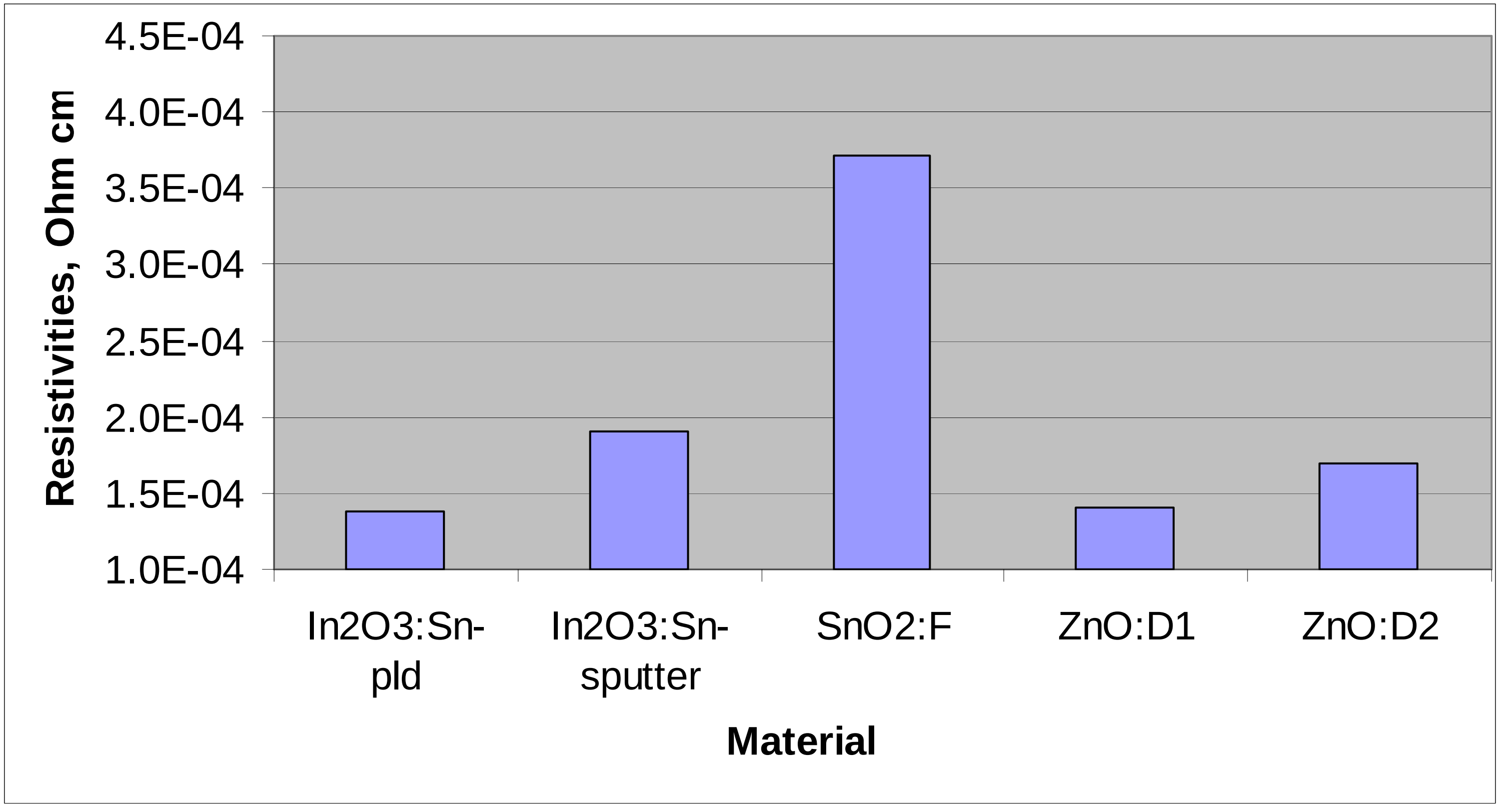
Introduction - Comparison of common TCOs



- Resistivities of 1.38 to 3.60 x 10^{-4} Ωcm are feasible
- Doped ZnO and ITO showed the lowest resistivity

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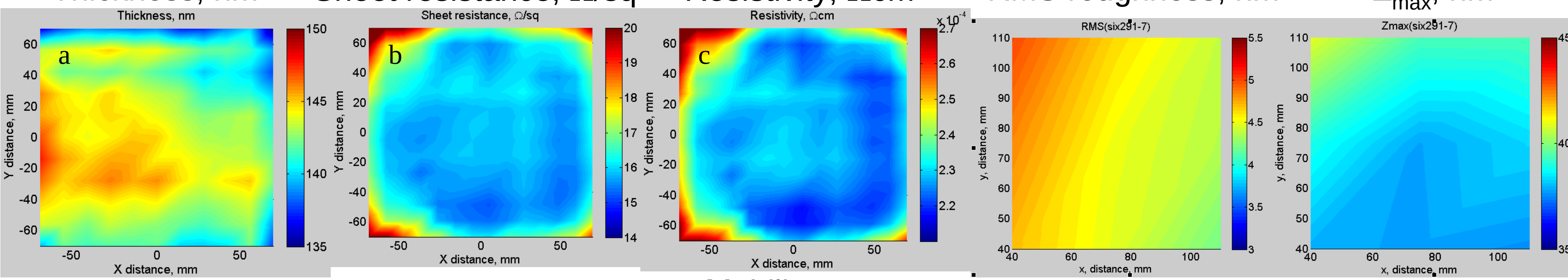
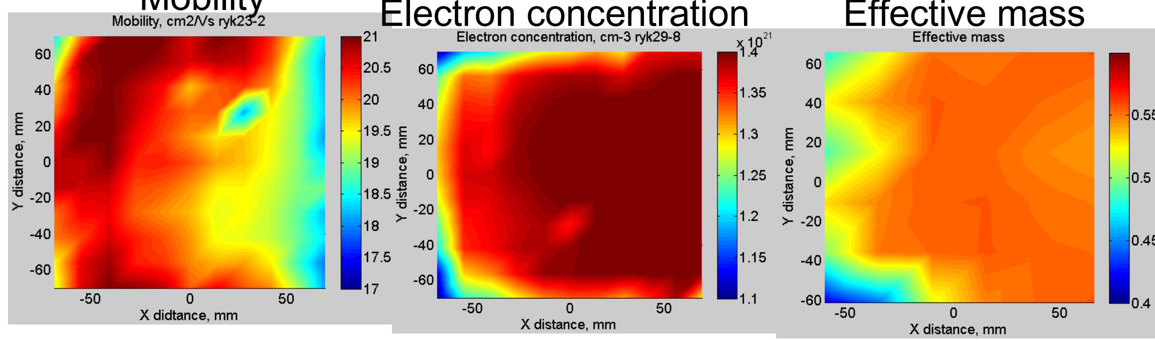
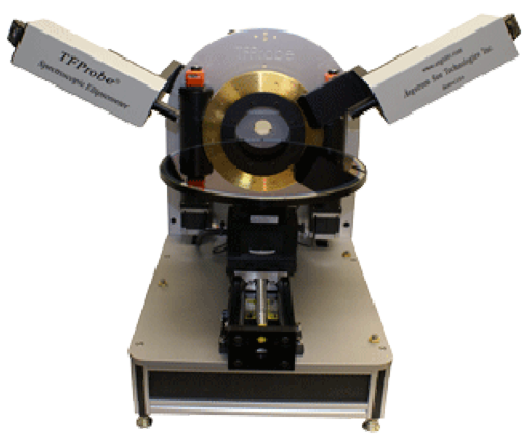
Homogeneity of DZO - Methodology

Thickness, nm | Sheet resistance, Ω/sq | Resistivity, Ωcm | RMS roughness, nm | Z_{max}, nm



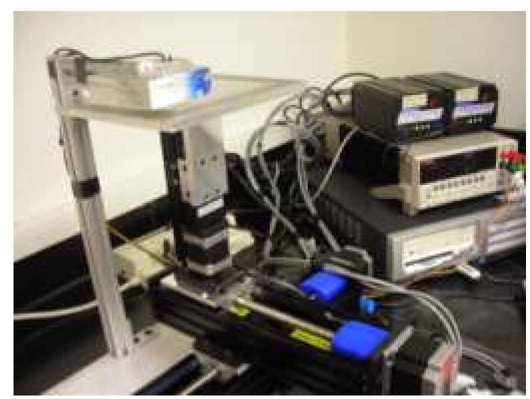
Mobility | Electron concentration | Effective mass





Spectroscopic ellipsometer

- 2D mapping of
  - Sheet resistance
  - Thickness
- Electron concentration
  - Electron mobility
  - Effective mass
  - RMS
  - Z_{max}



Automated 4-point probe

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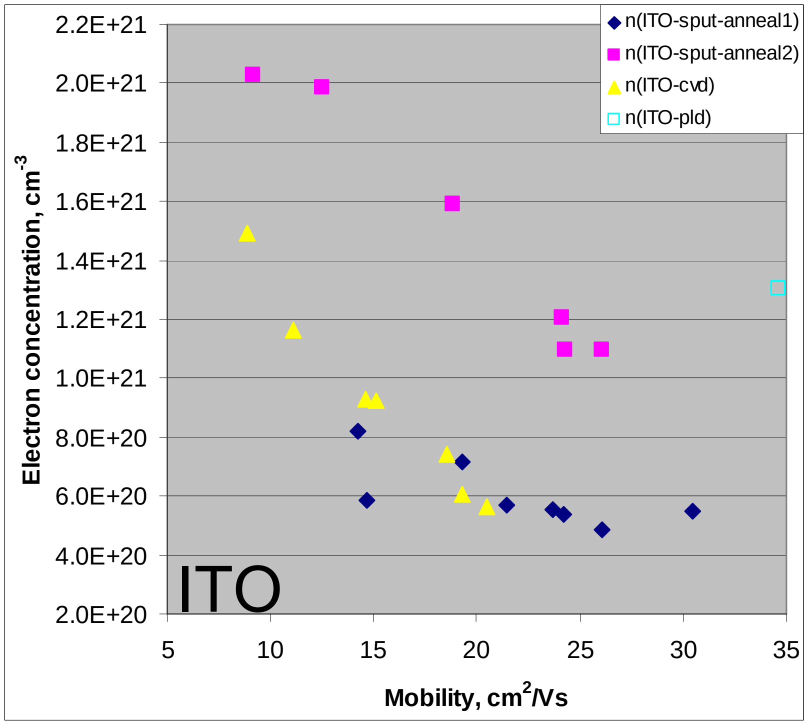
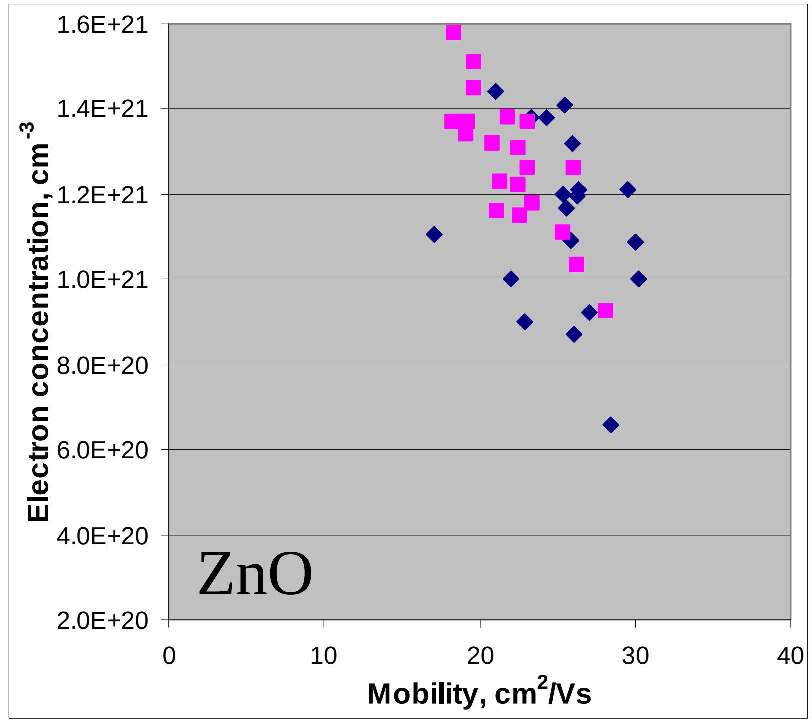
Electrical Properties - Electron concentration & mobility





- ITO electrical properties strongly depend on annealing conditions
  - As sputtered [Electron] and mobility of $6x10^{20}$ cm^{-3} and 15 cm^2/Vs
  - [Electron] increases to $2x10^{21}$ cm^{-3} with annealing
- Thick layers of DZO have similar electrical properties
  - Unintentially doped ZnO mobility = 50-55 cm^2/Vs
  - Doping reduces mobility to 12-30 cm^2/Vs
  - Electron concentration varies from 0.6 to 1.6 x 10^{21} cm^{-3}

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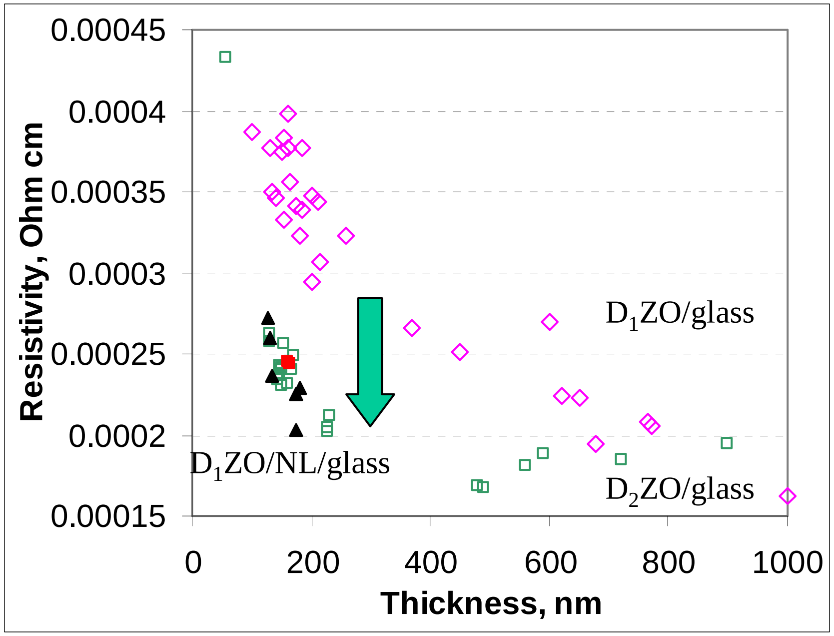
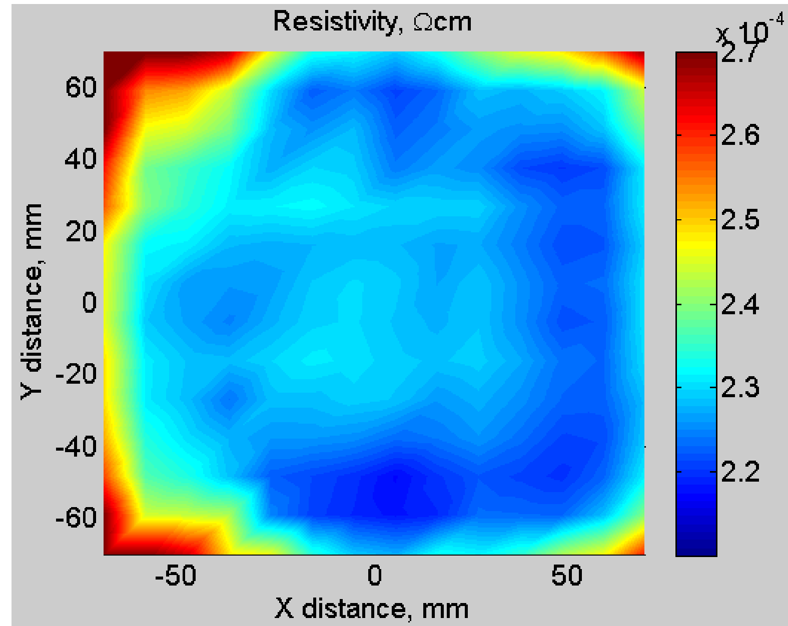
Electrical Properties - Resistivity





- Resistivity homogeneity ± 3 % over 6 x 6 inch surface.
  - Temperature gradients likely responsible for higher resistivity at edges
  - Lab coater uses a heating block versus even heat distributed oven

- APCVD deposited DZO resistivity correlates with film thickness
  - This correlation can be minimized by introduction of nucleation layer
  - This correlation can also be minimized by dopant type

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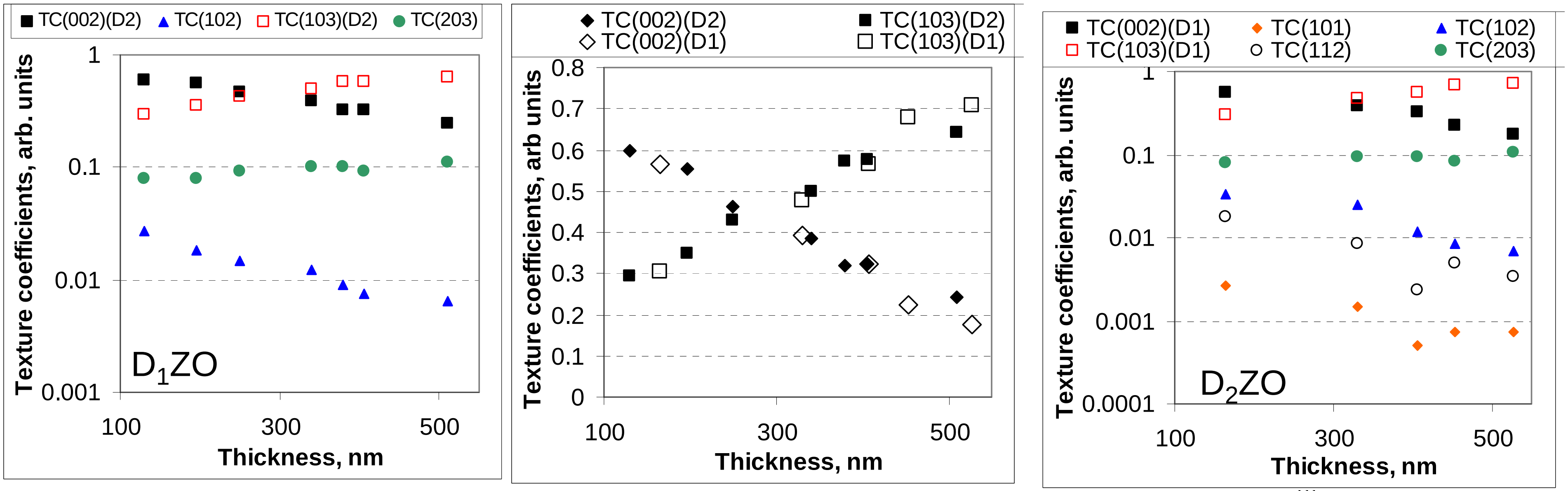
Depth Profiling – DZO texture coefficients



- Grazing angle X-ray intensities were corrected for thickness: $I_c^{hkl} = \dfrac{I_m^{hkl}}{1-\exp\left[-\left(\dfrac{\mu}{\rho}\right)\times\rho\times t\times\left(\dfrac{1}{\sin\alpha}+\dfrac{1}{\sin(2\theta-\alpha)}\right)\right]}$
- The texture coefficient is $TC(hkl) = \dfrac{I_c^{hkl} / I_0^{hkl}}{\sum_N I_c^{hkl} / I_0^{hkl}}$

$\rightarrow$ (002) Orientation is predominant at the glass/film interface
$\rightarrow$ (103) Becomes predominant orientation after 300 nm
$\rightarrow$ Crystallinity of D_1ZO and D_2ZO is similar

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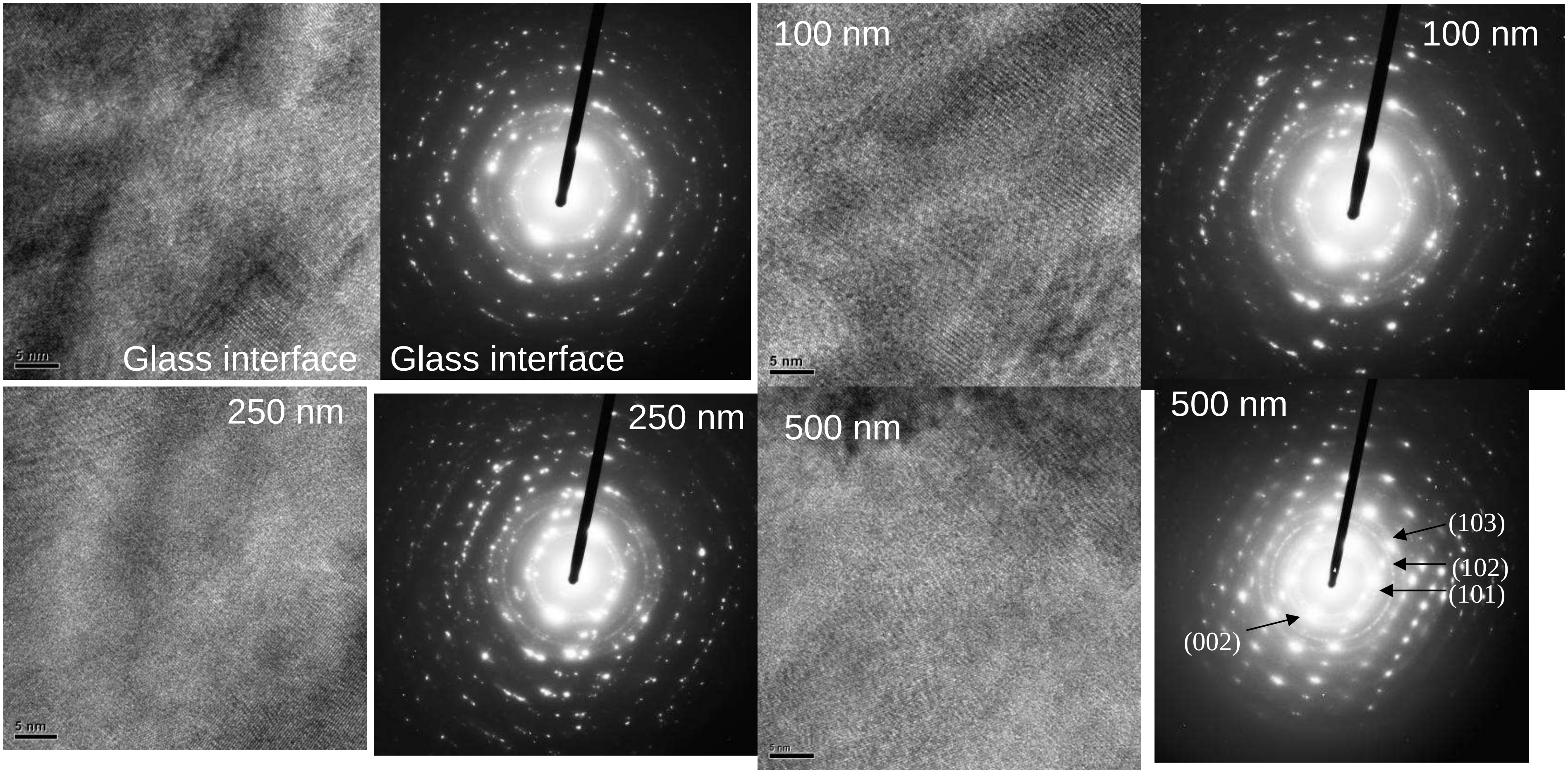
Depth Profiling - Crystallinity of doped ZnO by SAD



- The cross-section SAD show mostly polycrystalline orientation up to 500 nm
- The grains are rotated by 10-15 degrees with respect to each other
- (002), (103), (102) and (101) are found around 500 nm

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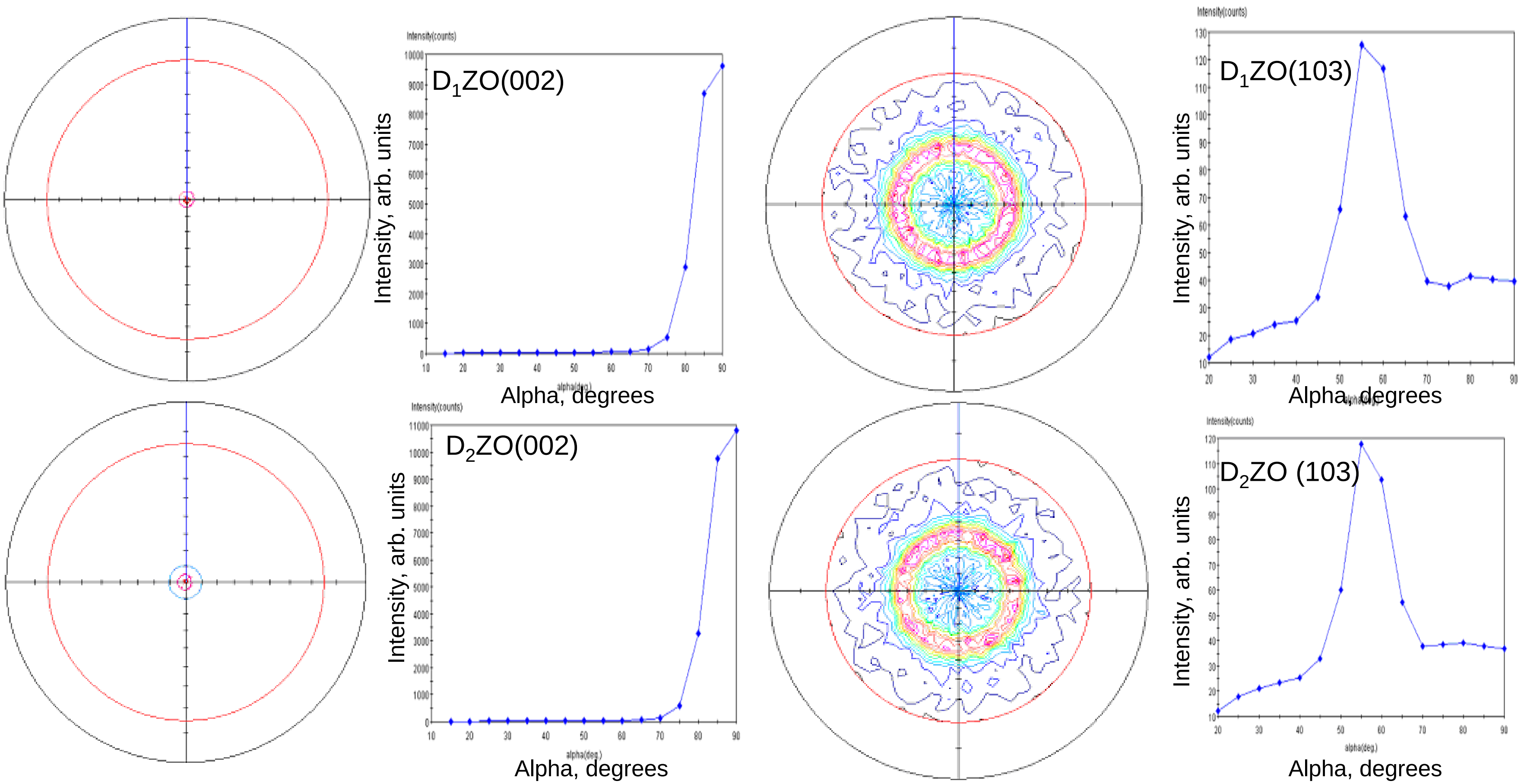
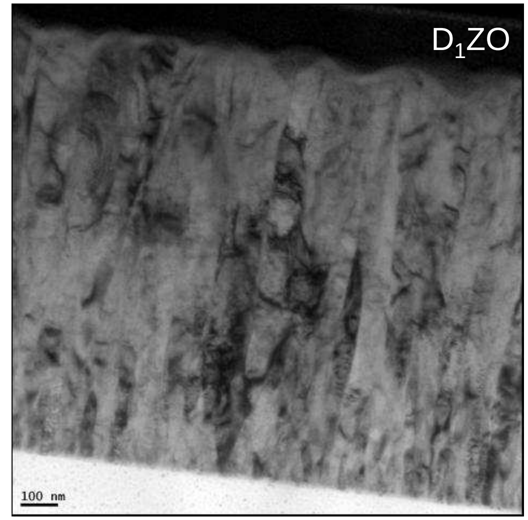
Depth Profiling - Pole figures for the bulk doped ZnO

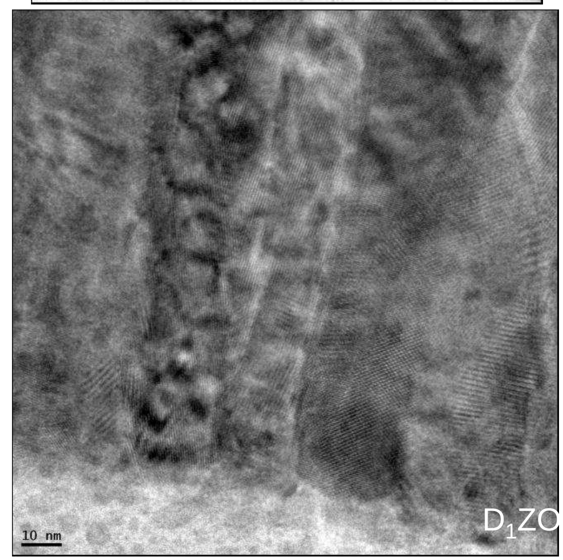


- Orientation factors (002) for $D_1ZO = 0.856$; $D_2ZO = 0.872$
  - (103) is 33±2° off the sample normal (002)
  - This angle corresponds to the 31.66° existing between (002) and (103)
  - The broad (103) signal increases towards the surface normal
- → ***As film thickness increases (103) aligns itself to the normal***

Depth Profiling - Crystalline sizes

Polish, #	0	1	2	3	4	5	6
(002), nm D_2ZO	67	74	69	72	73	69	63
(103), nm D_2ZO	29	32	30	30	30	29	29
Thickness, nm	510	406	380	340	250	196	130
Polish	0	1	2	3	4		
(002), nm D_1ZO	33	30	32	27	29		
(103), nm D_1ZO	17	16	15	14	14		
Thickness, nm	527	453	407	330	165		





- D_1ZO has 2x smaller grain size relative to D_2ZO
- Grain size decreases towards substrate interface
- Slope of mobility increase toward air:TCO interface

- The average grain size was calculated from grazing angle x-ray patterns (FWHM were corrected for IB):

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

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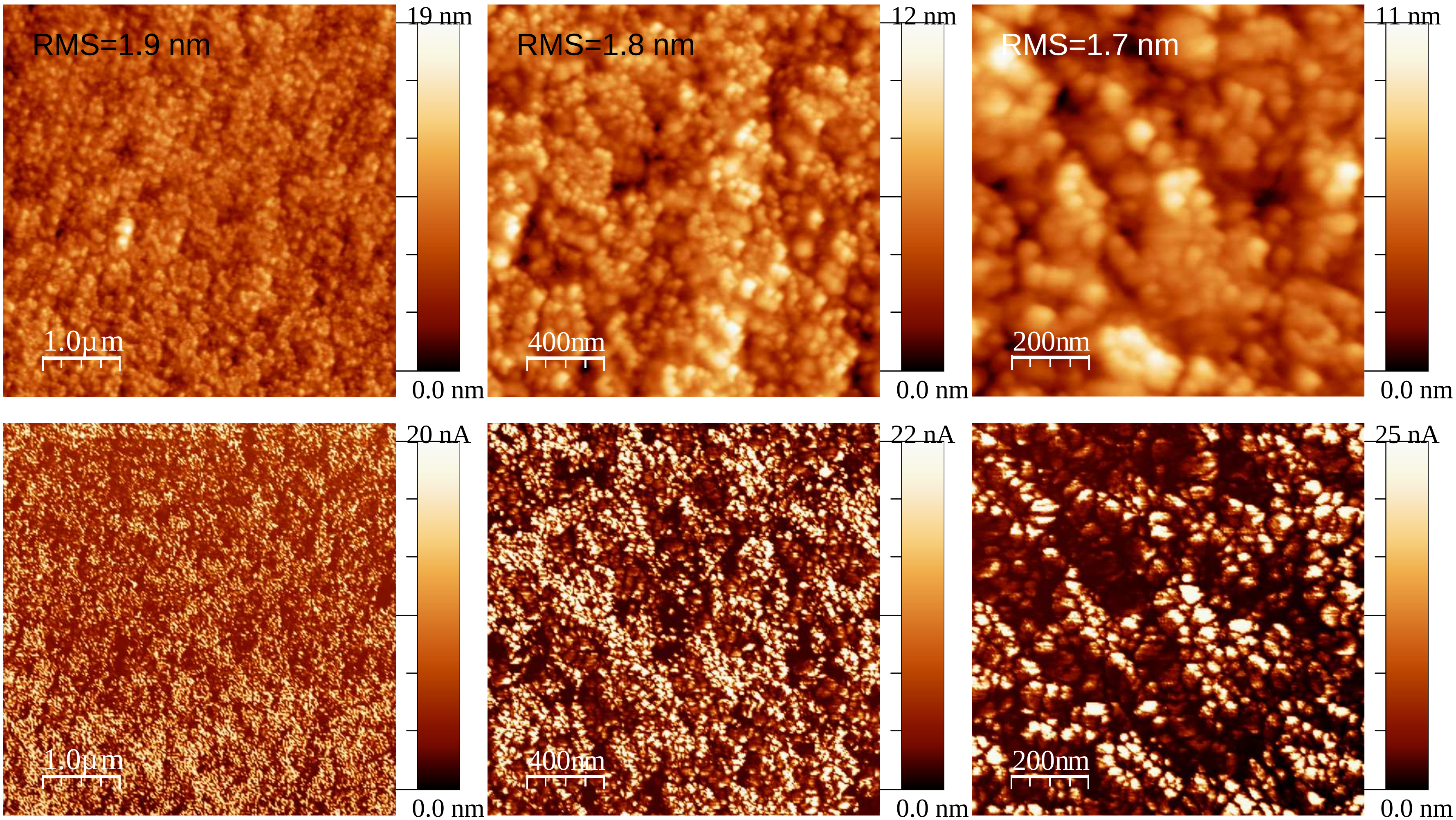
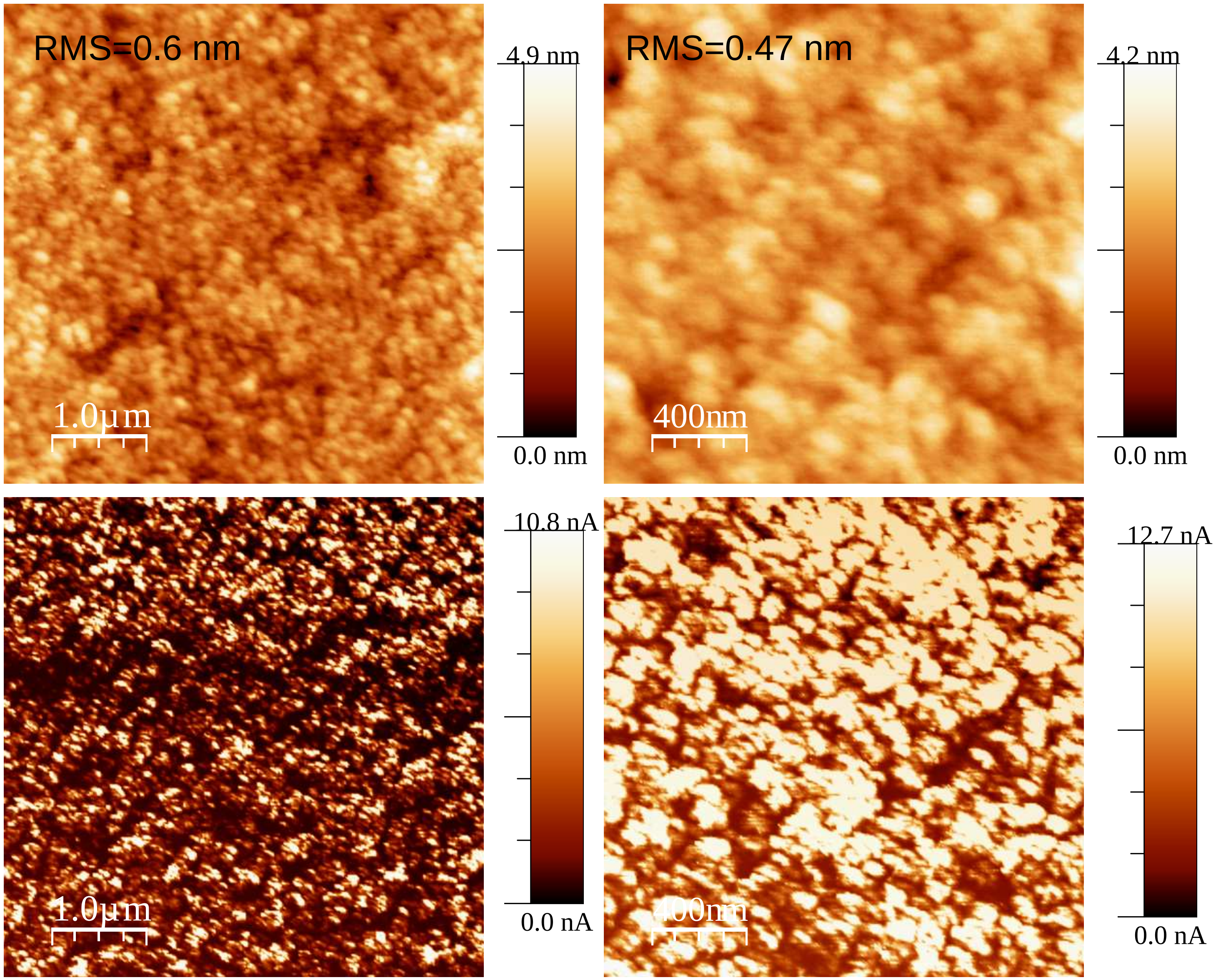
Current probe XY-profiles (ITO)

topography



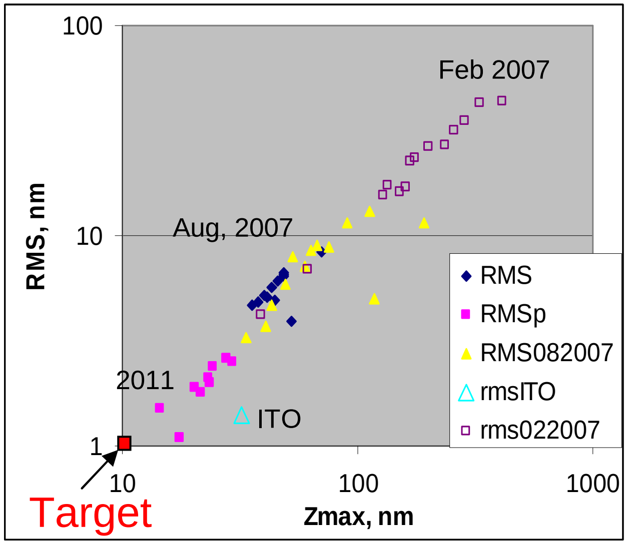
Current

Current probe XY-profiles (ZnO)

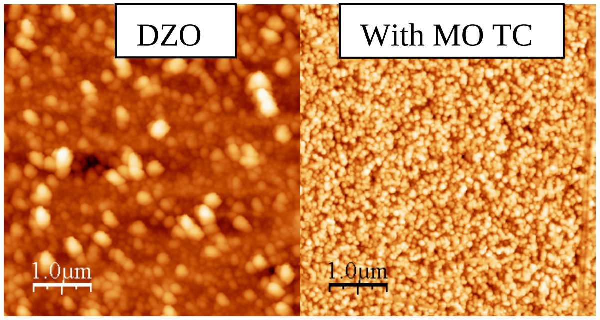


Surface roughness

- Deposition optimization – 50 % improvement
- HIL and p-doped layer as planarization tool
- Polishing (below RMS = 1 nm)
- Deposition of oxides as a planarization tool for DZO



#	Z_{max} (nm)	Rq (nm)	Ra (nm)	SR (Ω/sq)	TC thickness (nm)	φ (eV)
1a	278.8	22.7	16.8	5-8	None	5.0
2a	177.7	24.1	17.4	5-8	None	5.0
1b	64.7	9.1	7.4	5-8	10-20	--
2b	55	8.3	6.8	5-8	10-20	--



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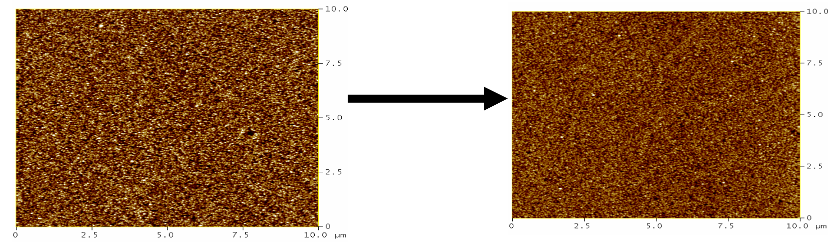
Surface Roughness - OLED Process Testing

1. 504 hr stability test 60 rh%:80°C both on substrate & metalized
   - D^1ZnO passes in covered areas, but exposed regions have electrical deterioration – not a knock out
   - D^2ZnO passes all around, but is more expensive
2. Process compatibility

ZnO substrates	rms
Without cleaning	3.6 - 3.8 nm
Acetone & propanol cleaning (each 5 min. ultrasonic bath)	3.0 - 3.3 nm
Cleaned and fully processed substrate	2.2 - 2.4 nm
Polished TCO and cleaned substrate	1.4 nm



As is — Solvent cleaned

- Cleaning done on- & off-line
- Solvent and surfactant compatibility identified
- Surface roughness decreased on cleaning
- No evidence of etching - cleaning surface particles
- Patterning process identified

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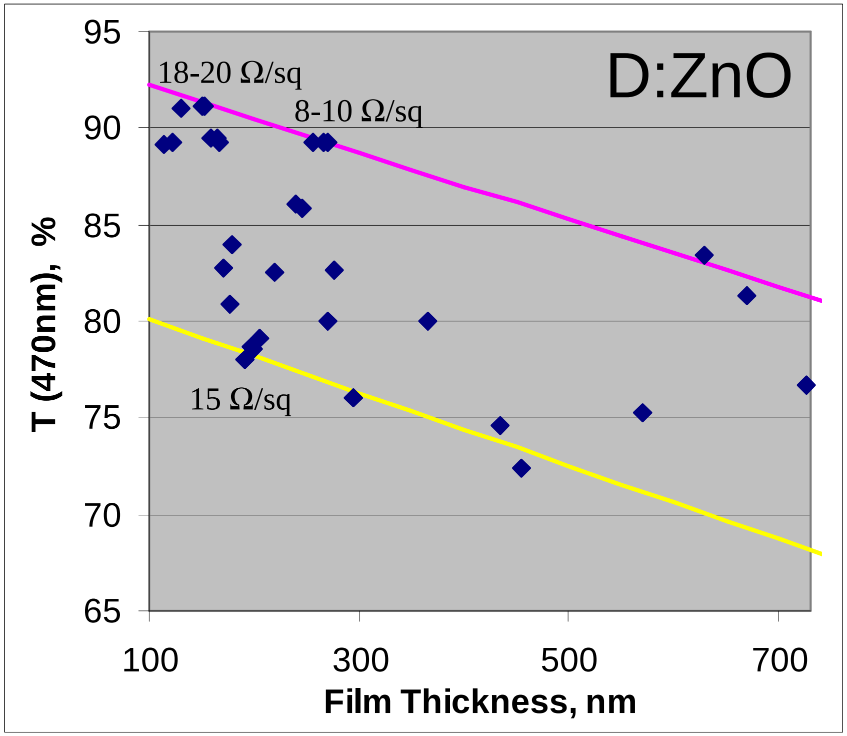
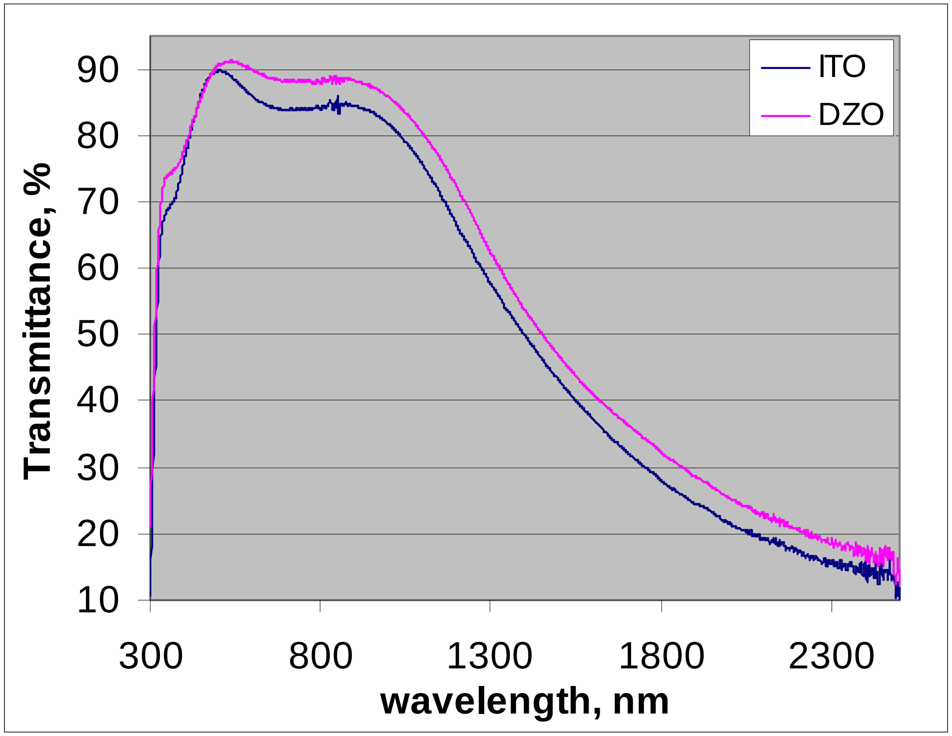
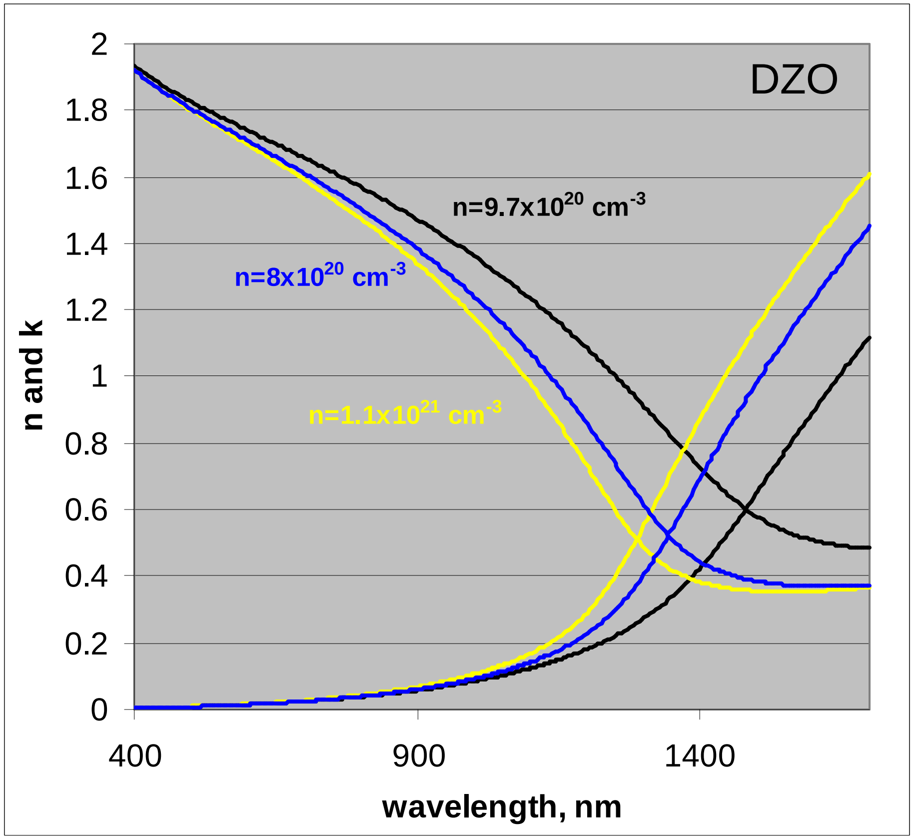
Optical properties

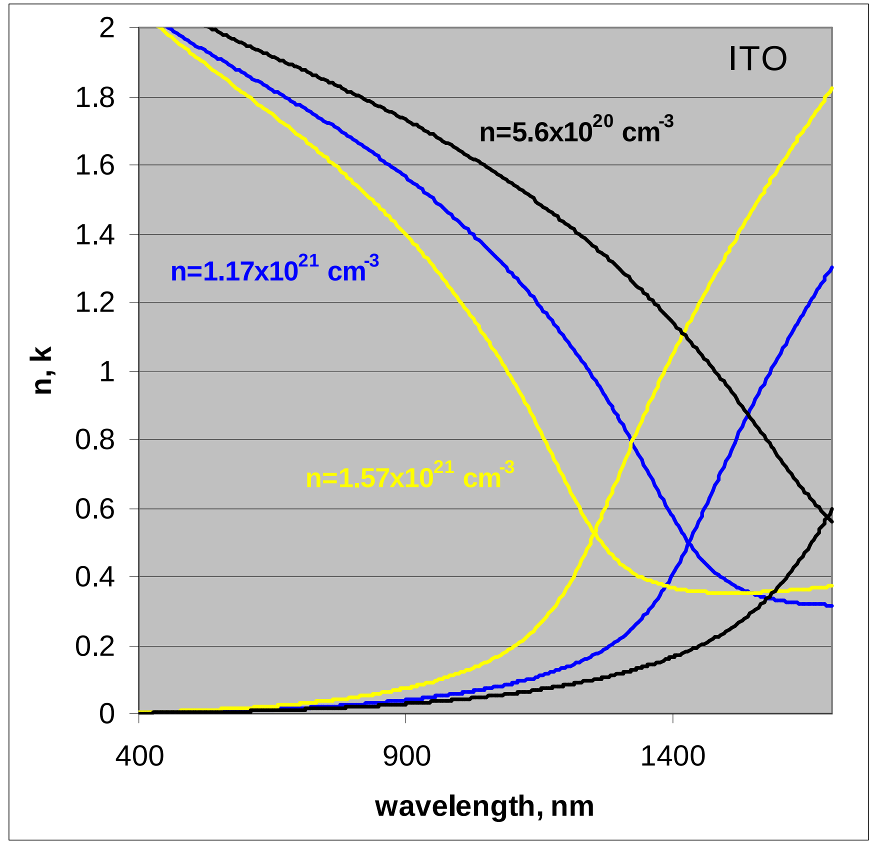




- Maximum transmittance of doped ZnO (150 nm) plus glass substrate was 91 %
- Transmittance of DZO was slightly better than ITO for the similar thickness thin films (< 200 nm)

Optical properties - N and k as a function of doping





- Dispersion curves for both ZnO and ITO are dependent on doping level
- Dispersion curves were utilized in development of the undercoat

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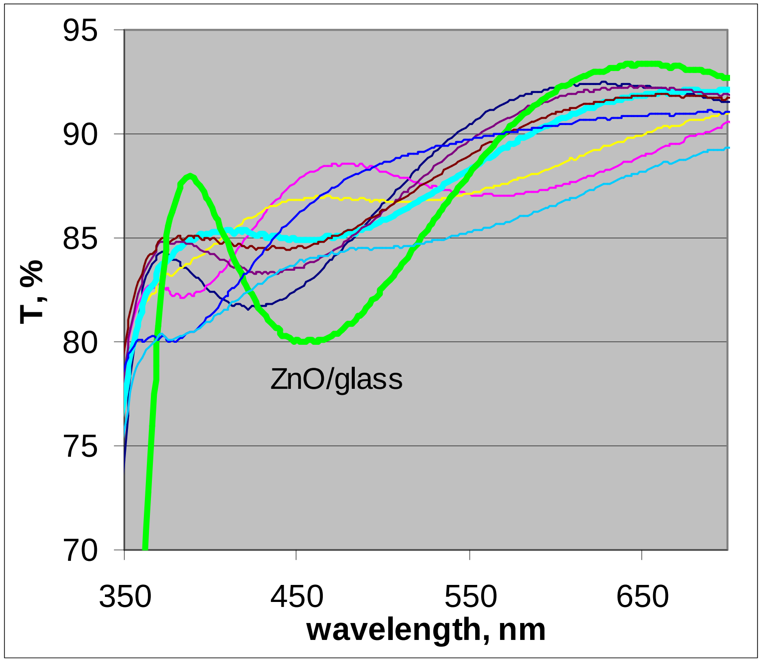
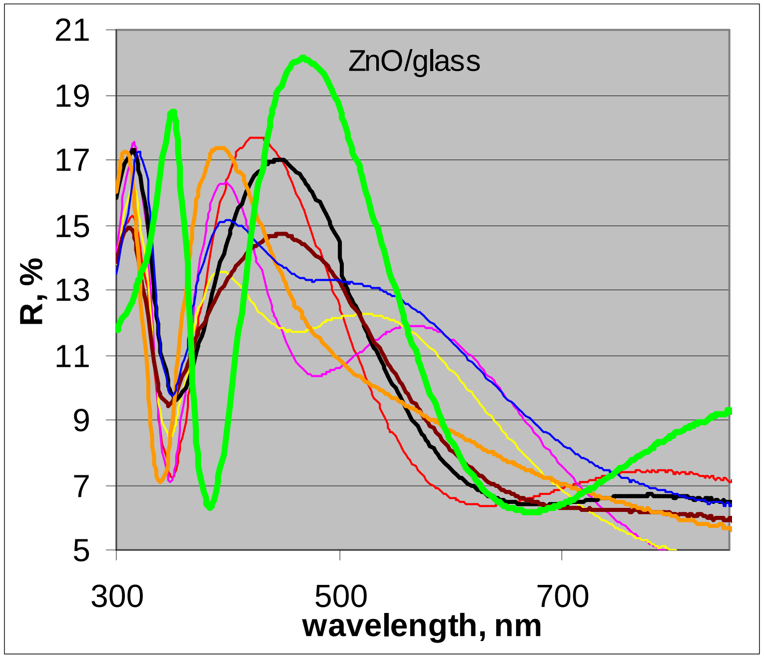
Light Out-coupling - Refractive index matching





- Undercoat technology using APCVD grown layers was developed
- Peak reflected interference fringe for DZO → 20% to 13-14%
- Flat transmittance curves with suppressed Fabry-Perrot interference are obtained using undercoats

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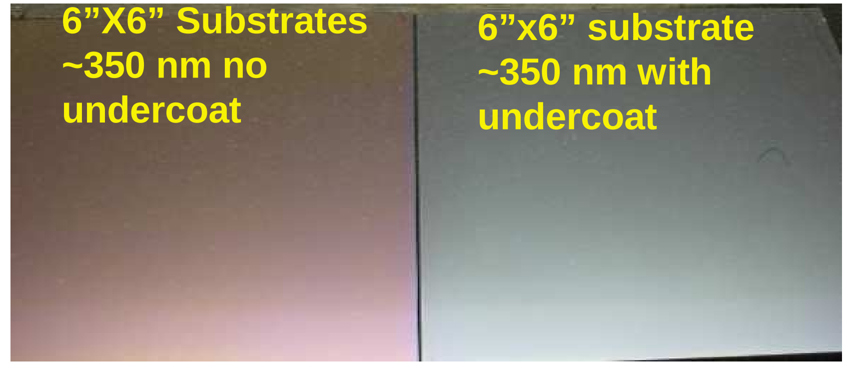
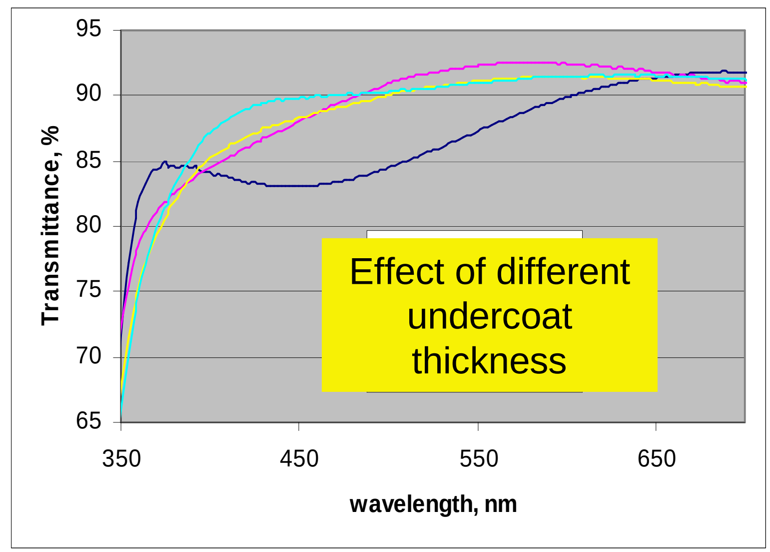
Light Out-coupling – Approach 1

Undercoat for Optical Extraction

- **Optical UC**
  - Improves transmission 2-5%
  - Improves EQE 9-11%



Sample	HIL, nm	V	EQE, %	Change, %
DZO	HIL[1](30 nm)	3.8	12.0	-
DZO/UC	HIL[1](30 nm)	3.8	13.4	11.6
DZO	HIL[2](35 nm)	4.0	12.1	-
DZO/UC	HIL[2](35nm)	4.0	13.2	9.1
ITO	HIL[1](30 nm)	3.9	14.8	-
ITO	HIL[2](35 nm)	4.4	15.2	-



* - Blue OLEDs prepared and analyzed at PNNL

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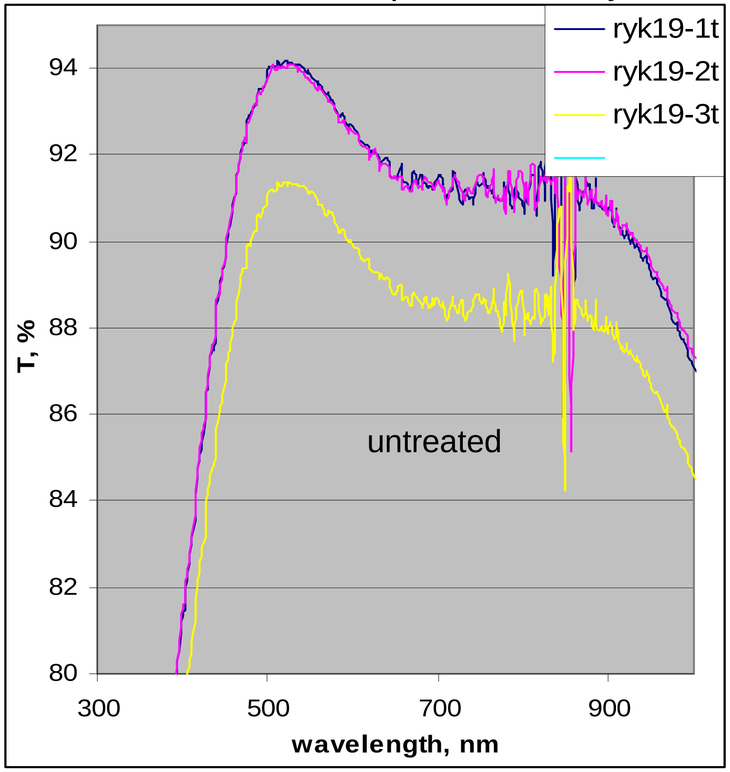
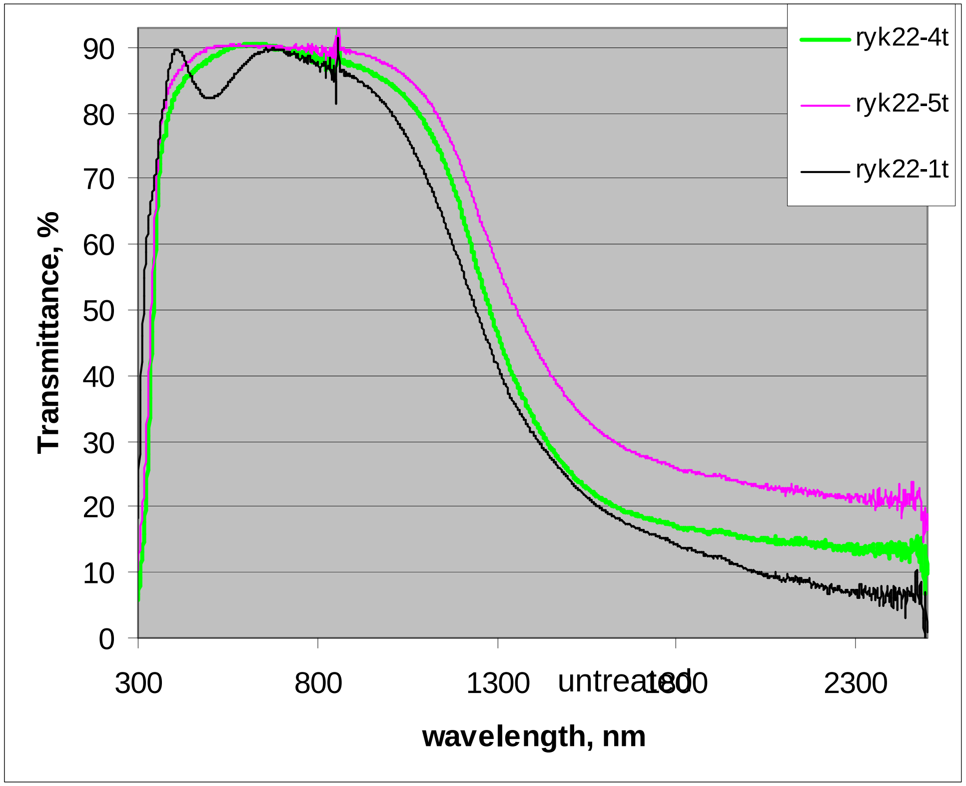
Light Out-coupling - Approach 2

GZO on patterned glass substrates

Substrate backside patterned only



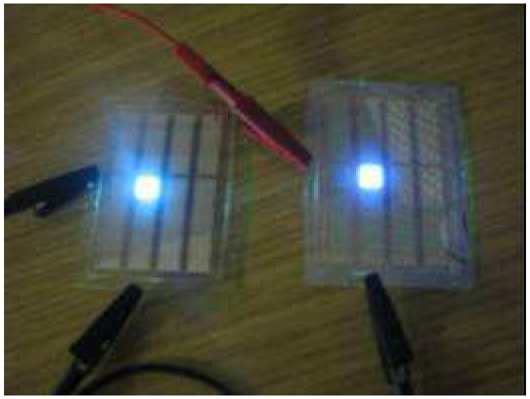
Substrate front side patterned only



- Average 3 % improvement in overall transmission was observed for patterned substrate backside
- An overall flat transmittance curve was observed for the patterned front side of the substrate

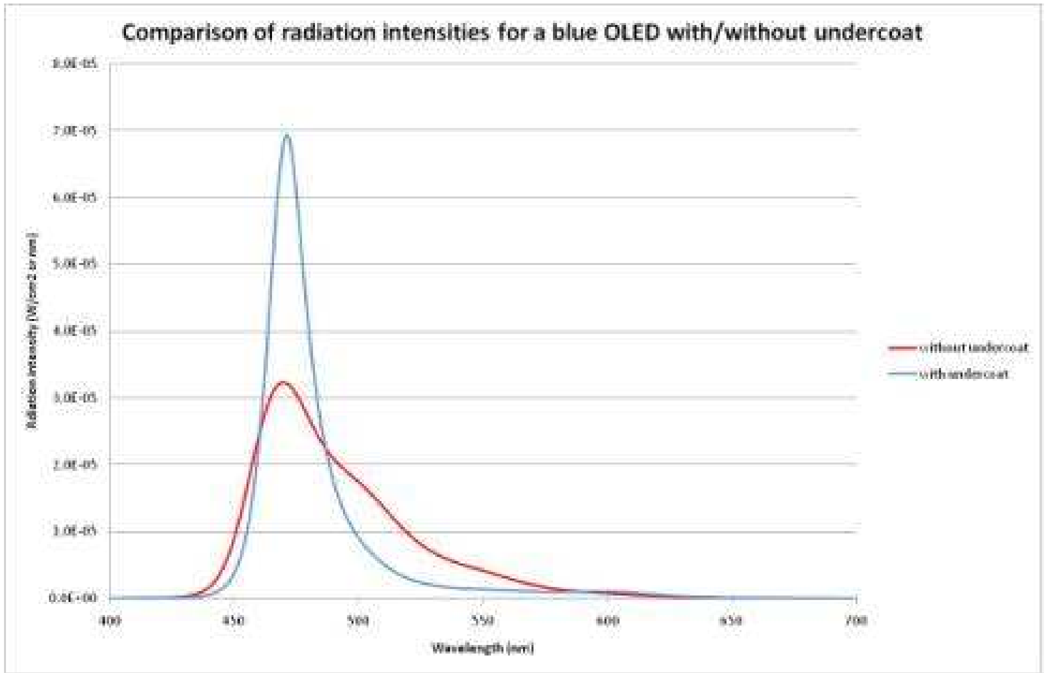
Light Out-coupling Approach 3

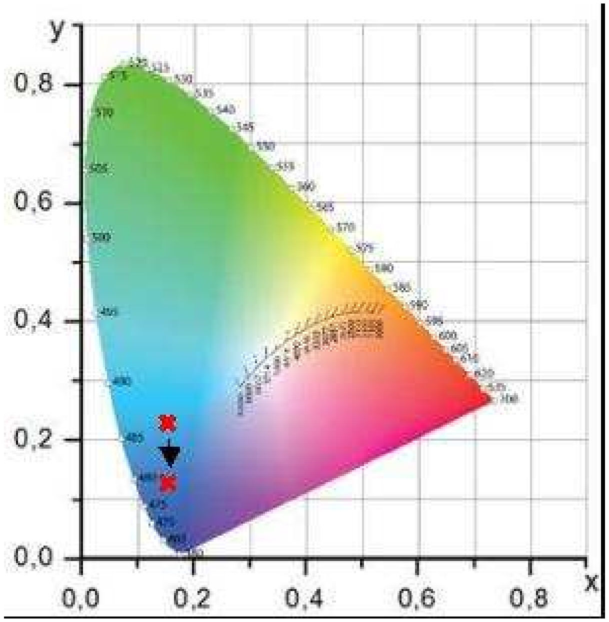
Light extraction



High-low-high RI ($Nb_2O_5/SiO_2/Nb_2O_5$/DZO)

- Enhancement emission amplitude of 2.6x (theory) and 2.1x (experimental) at 475 nm
- Effect falls off at >10^0 and very tight process window
- Color shift to deeper Blue

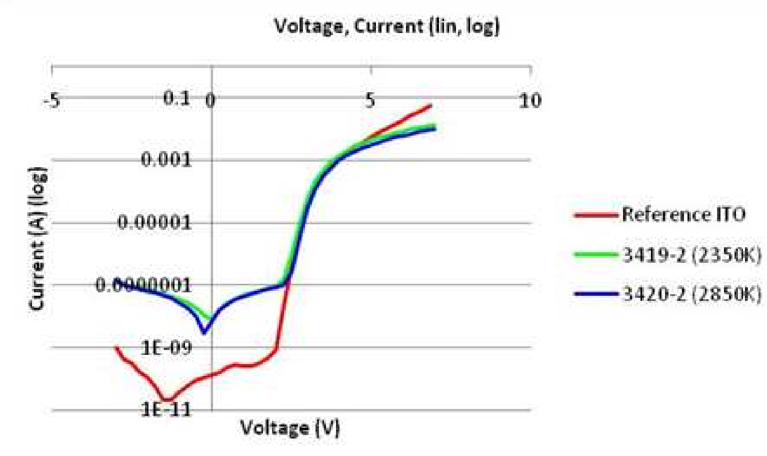


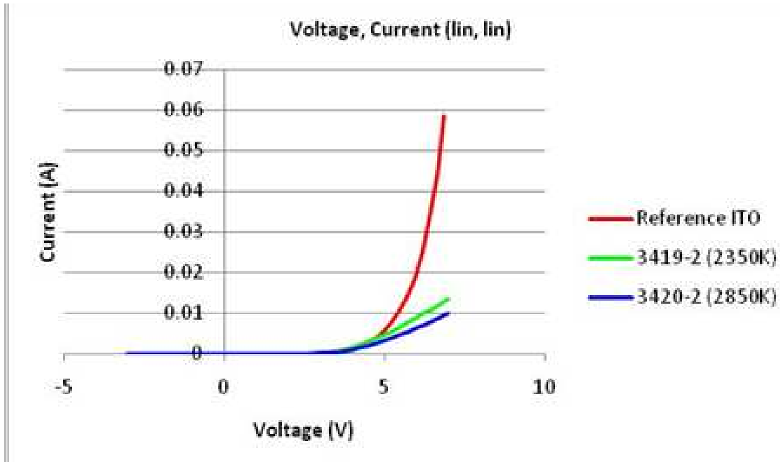


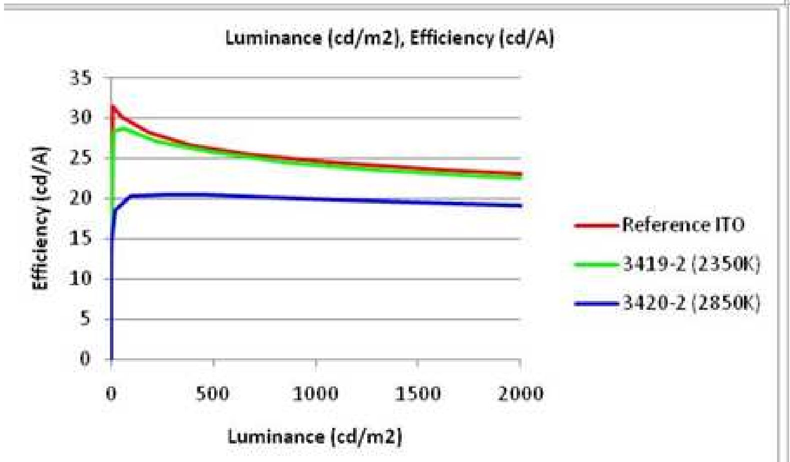
OLED Devices and analyses done at Philips Lighting

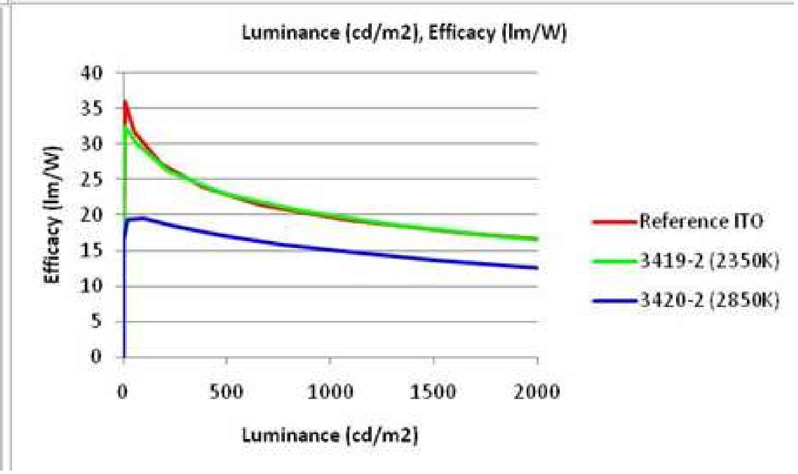
OLED Devices- 5x5 mm^2 device made on 6” substrates

Results comparable to ITO for small pixel size (5mm x 5mm)





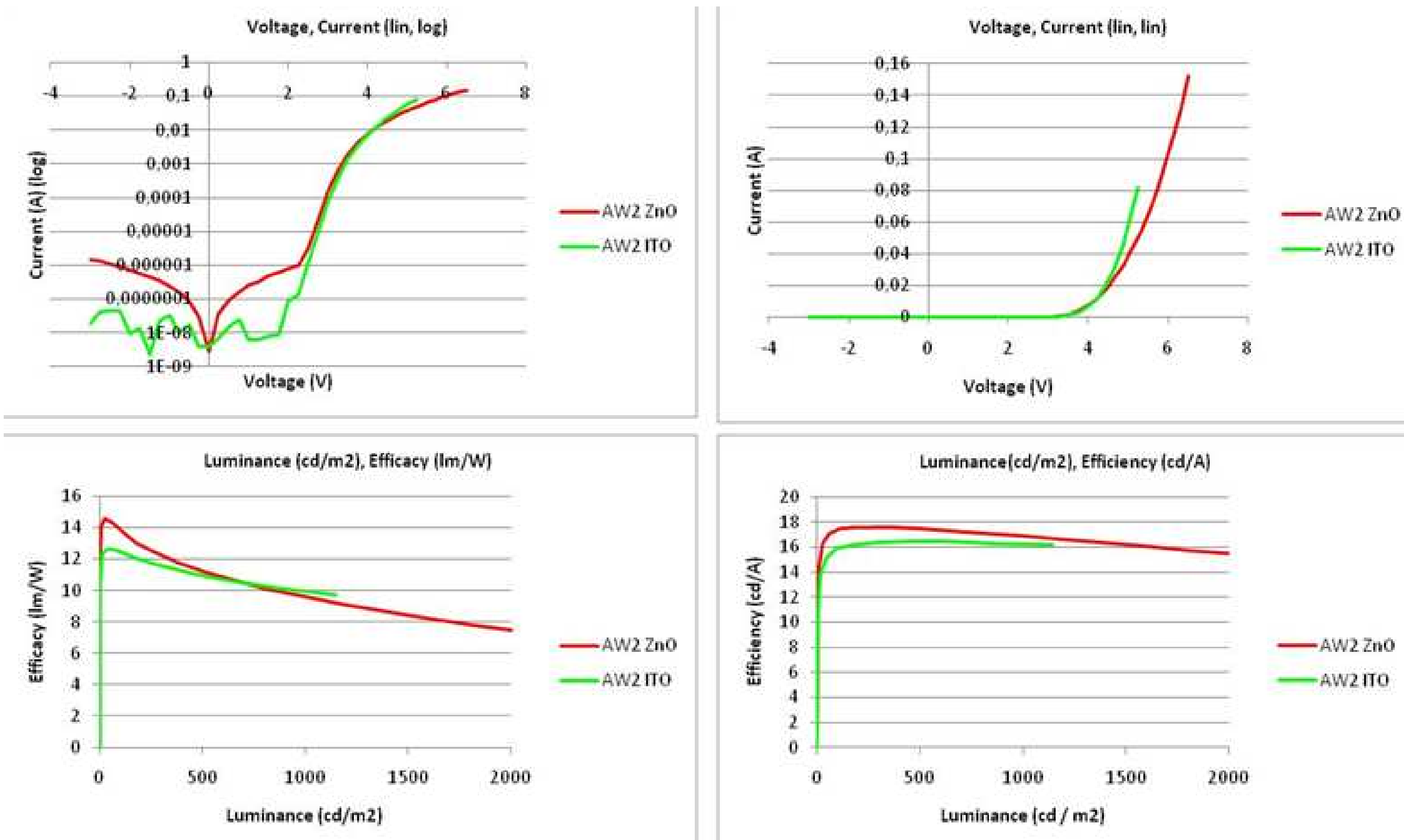




OLED Devices and analyses done at Philips Lighting

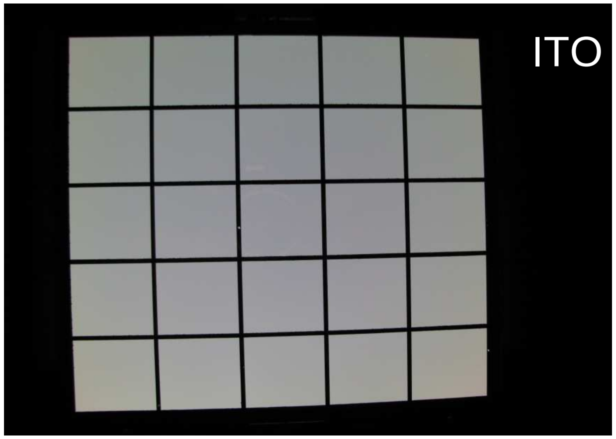
OLED Devices - scale-up to 30x40 mm²

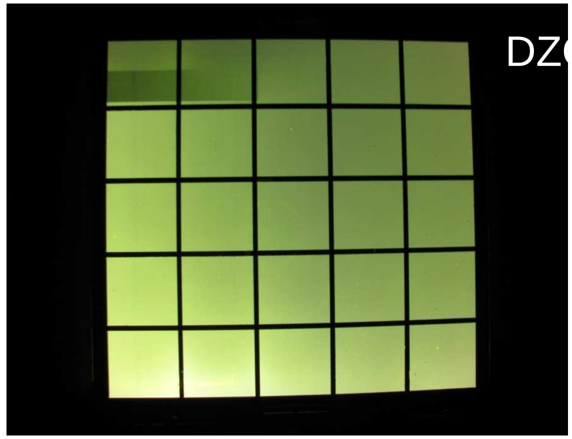
Results comparable with ITO for larger OLED design

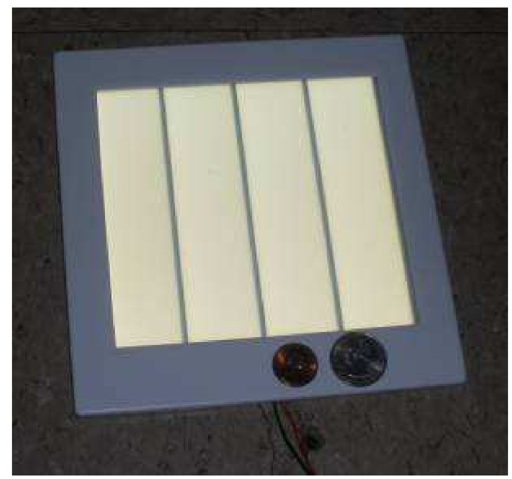


OLED Devices and analyses done at Philips Lighting

OLED Devices - 152x152 mm^2 full substrate







- Processing is simplified in serial construction
- More work is needed for Grid construction
- Demonstrate DZO can be used as TCO

Conclusions

- APCVD prepared doped ZnO is a viable commercial alternative to ITO
  - Demonstrated 5x5, 30x40 and 152x152 mm^2 devices
- Dopants and process conditions are critical to homogeneity and opto-electronic properties
- Projected cost for DZO are consistent with DOE SSL 5-year plan targets

	Trans. (%)	Ion Migration	SR	W_f (eV)	RMS (Z_{max})	Acid resistance
DZO	> 90%	No	17-20	4.8-5.0	4(30)	No
ITO	> 85%	Yes	17-20	4.6-5.0	2(20)	Yes

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