ZnO:Al Doping Level and Hydrogen Growth Ambient Effects on CIGS Solar Cell Performance

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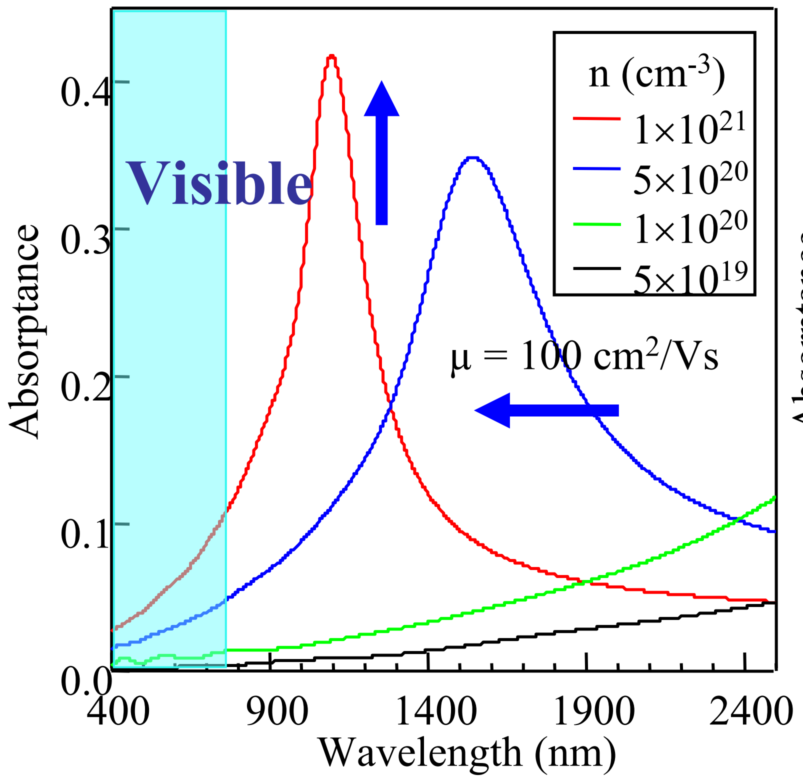
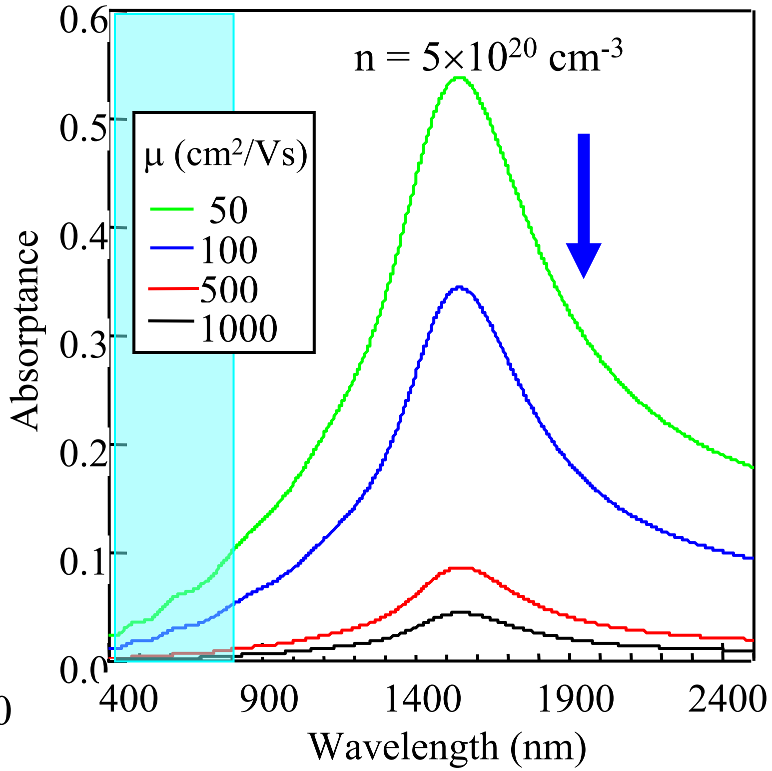
Modeled TCO Absorptance

Varying carrier conc.



Varying mobility



A=1-T-R

$$\sigma = qn\mu$$

$$\omega_p = \frac{2\pi}{\lambda_p} = \sqrt{\frac{4\pi ne^2}{m^*}}$$

T. Coutts *et al.*, MRS Bulletin **25**, 58 (2000)

Best optical properties by increasing mobility rather than carrier concentration

Investigations in this study

ZnO:Al Studies

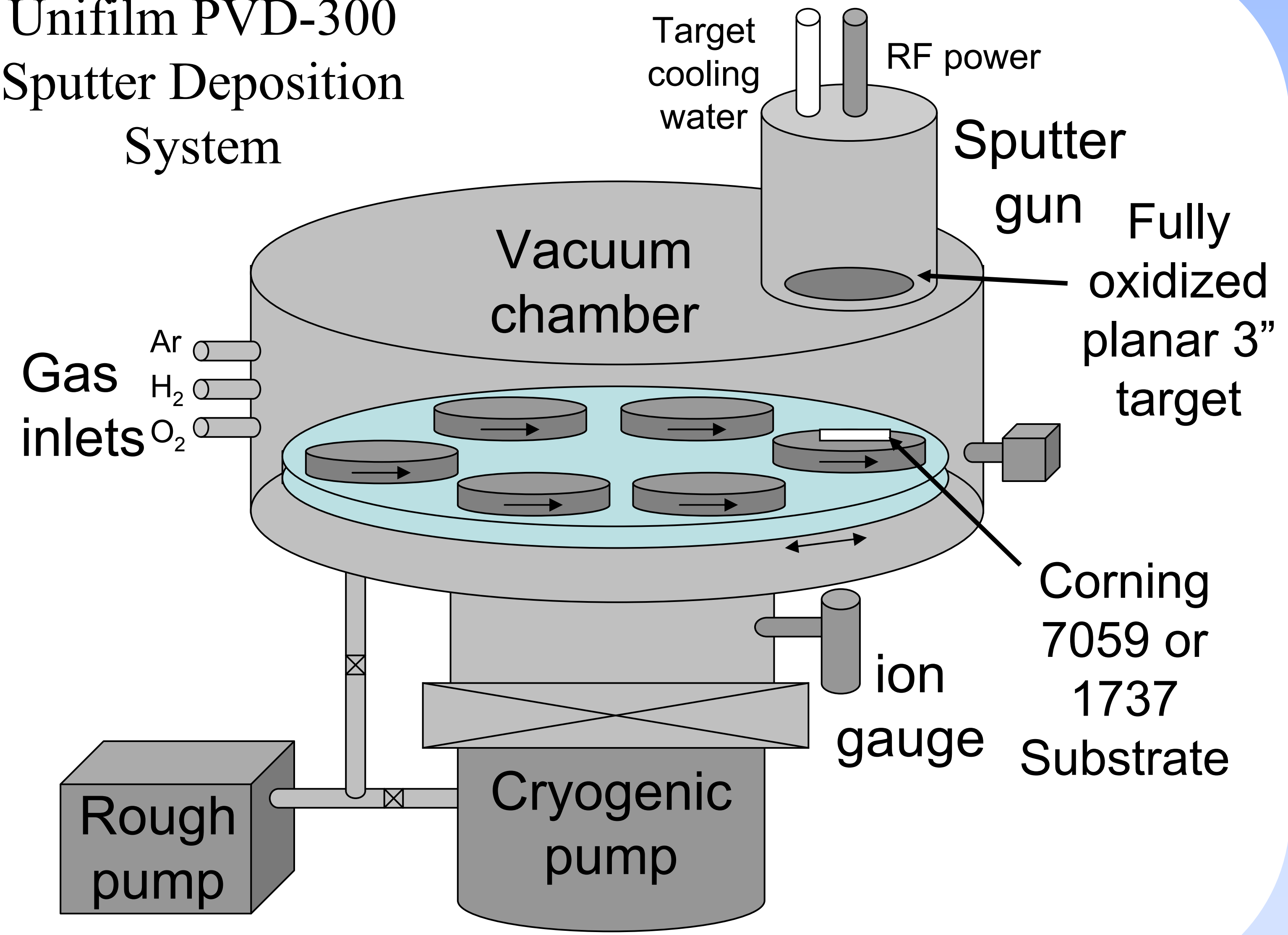
- ZnO:Al with 2.0 wt.% Al_2O_3 commonly used, but limits carrier mobility
- We investigate lightly-doped ZnO:Al grown using small amounts of H_2 in the Ar sputtering ambient
  - 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 wt.% Al_2O_3

CIGS PV Device Studies

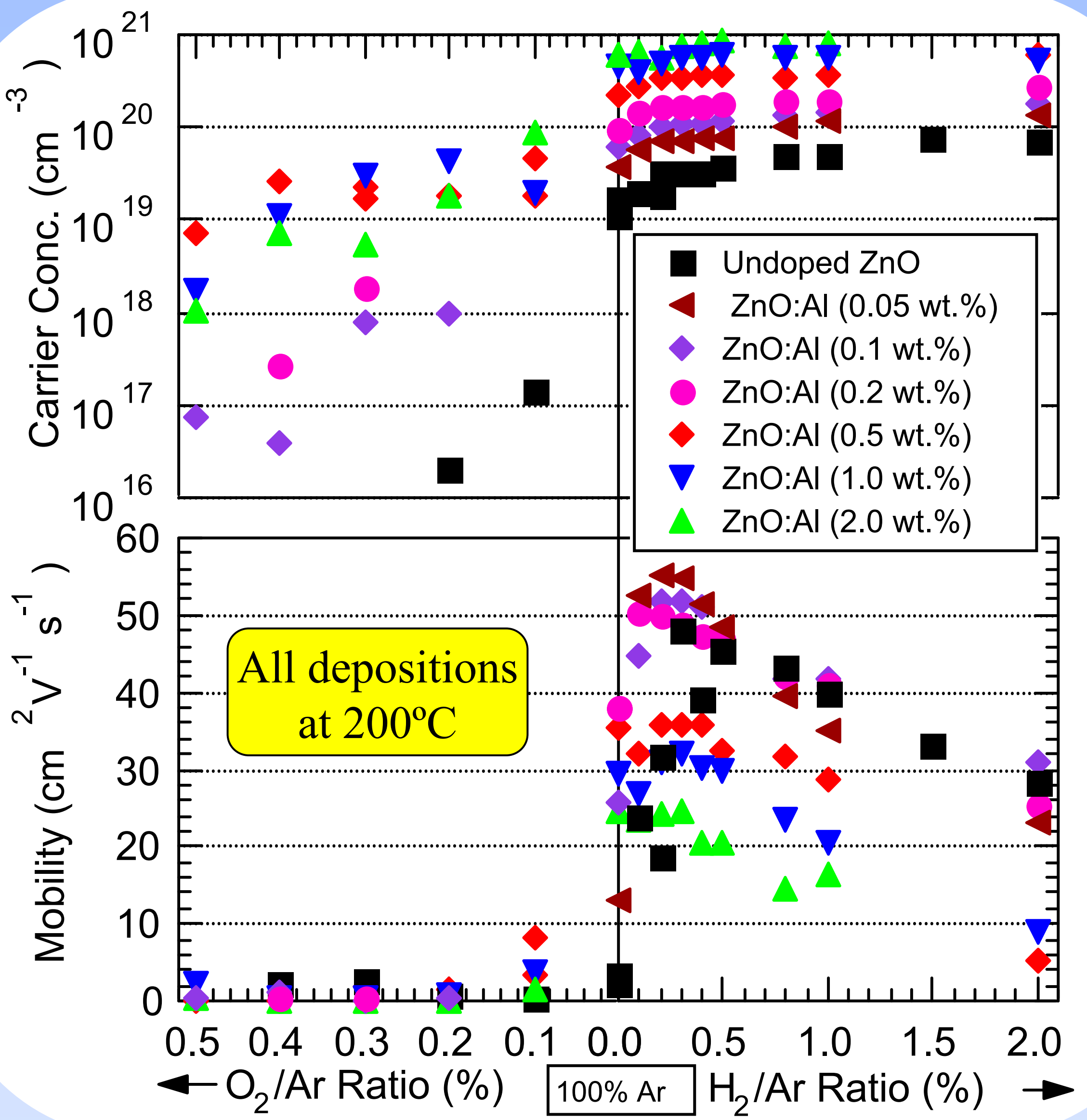
Compare CIGS PV devices with lightly-doped and standard ZnO:Al (0.1 wt.% Al_2O_3 vs. 2.0 wt.% Al_2O_3)

Film Growth

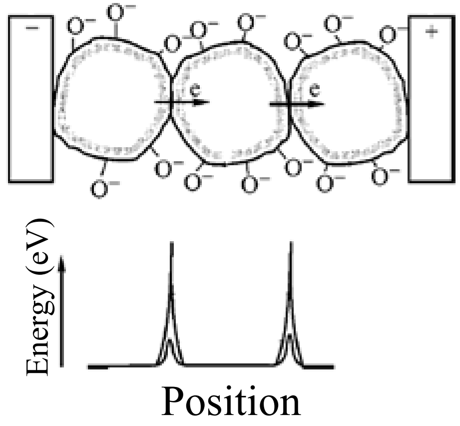
Unifilm PVD-300
Sputter Deposition
System



Electrical Data - Ambient Studies



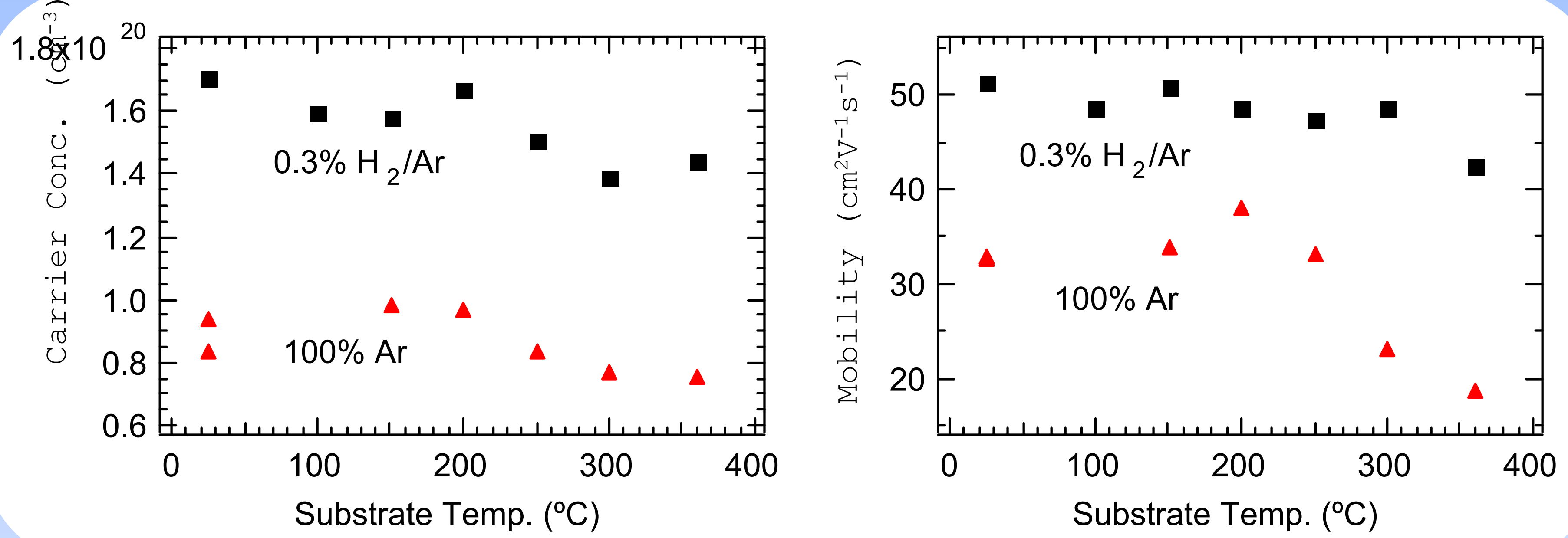
- Adding O_2 sharply decreases both carrier concentration and mobility
- Adding H_2 in limited amount is beneficial to both



Gaskov *et al.*, Rus. J. Appl. Chem. **74**(3), 440 (2001)

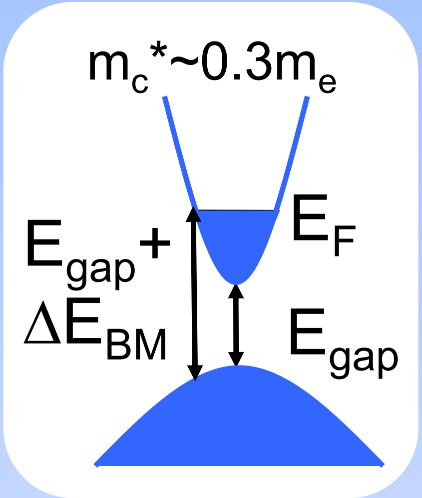
Electrical Data - Substrate Temp. Series

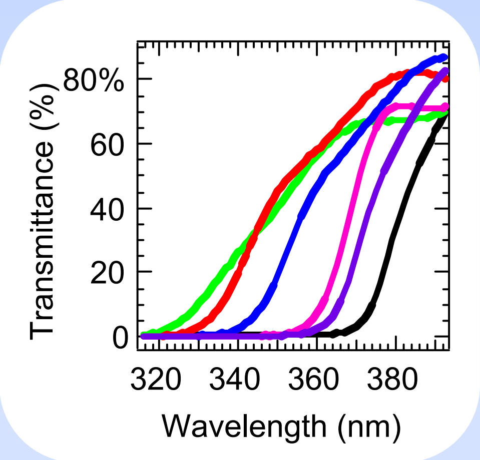
100% Ar and 0.3% H_2/Ar, 0.2 wt.% Al_2O_3



- 100% Ar peaks at ~150-200°C
- Slight monotonic decrease for 0.3% H_2/Ar
- Tolerance for higher substrate T with H_2 added

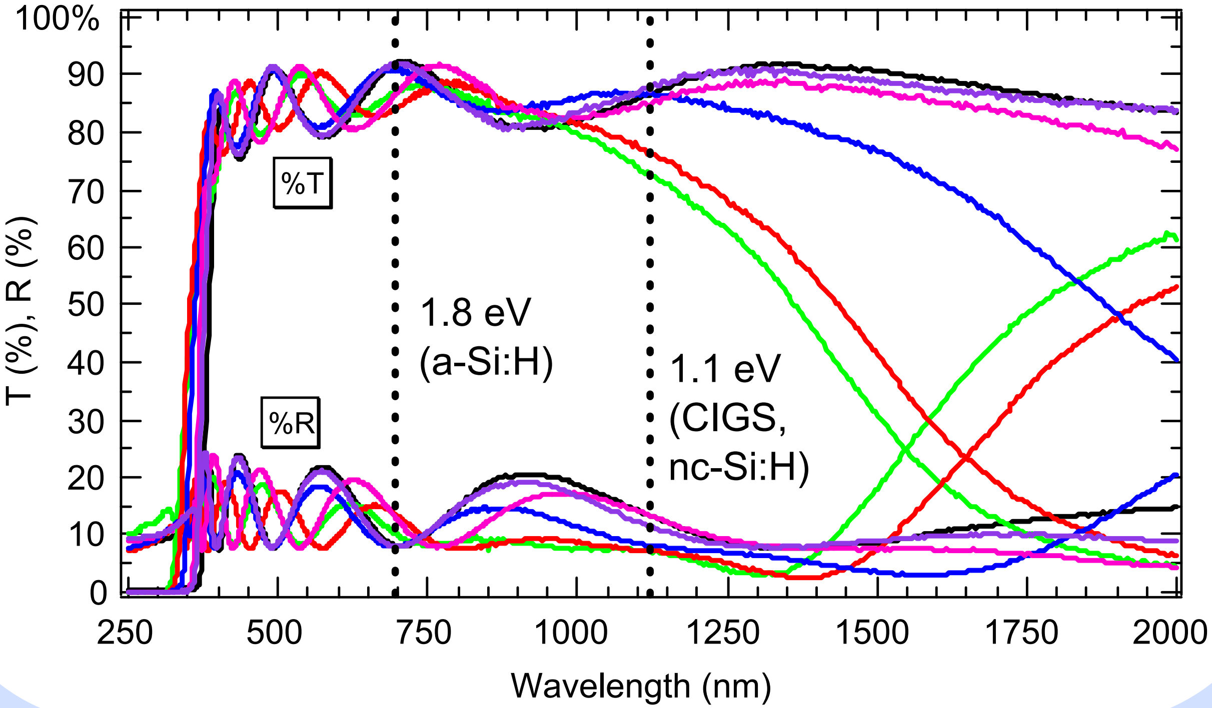
Optical Data





Best optical properties for ZnO-based films, substrate temp. 200ºC

	Thick. (nm)	n (cm^{-3})	μ (cm^2/Vs)	ρ (ž cm)
— Undoped ZnO	390	3.3×10^{19}	48	4.0×10^{-3}
— ZnO:Al (0.1 wt.%)	370	1.1×10^{20}	52	1.1×10^{-3}
— ZnO:Al (0.2 wt.%)	420	1.7×10^{20}	49	7.7×10^{-4}
— ZnO:Al (0.5 wt.%)	410	3.4×10^{20}	36	5.1×10^{-4}
— ZnO:Al (1.0 wt.%)	490	5.5×10^{20}	32	3.6×10^{-4}
— ZnO:Al (2.0 wt.%)	470	5.9×10^{20}	25	4.3×10^{-4}



- Burstein-Moss shift observed
- Free-carrier absorption in infrared

CIGS PV Device Studies

Control:

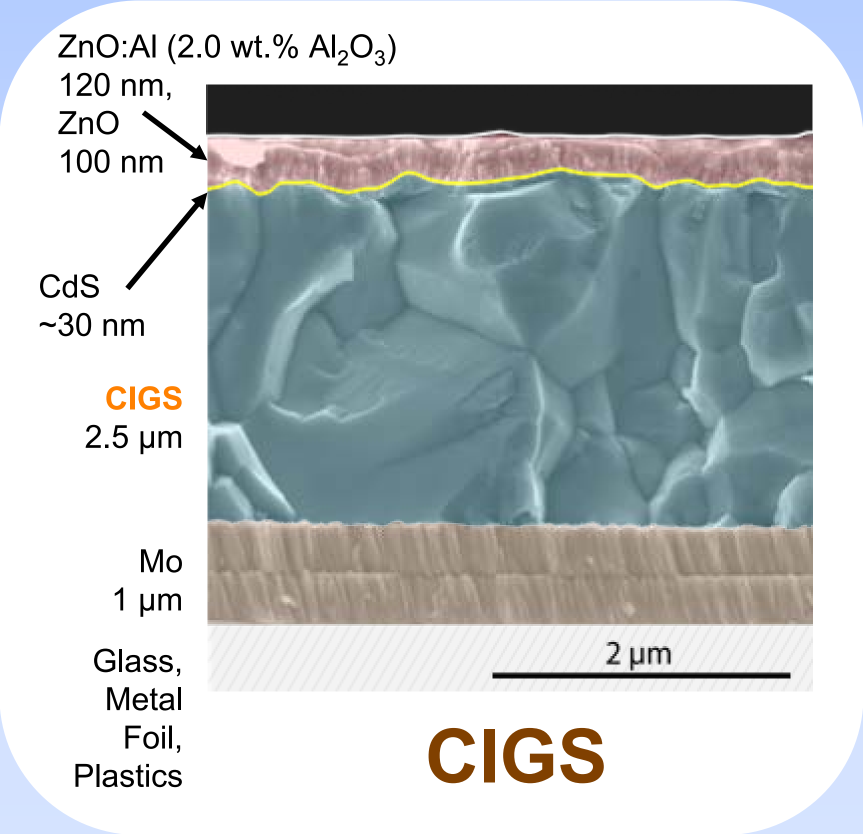
2.0 wt.% Al_2O_3

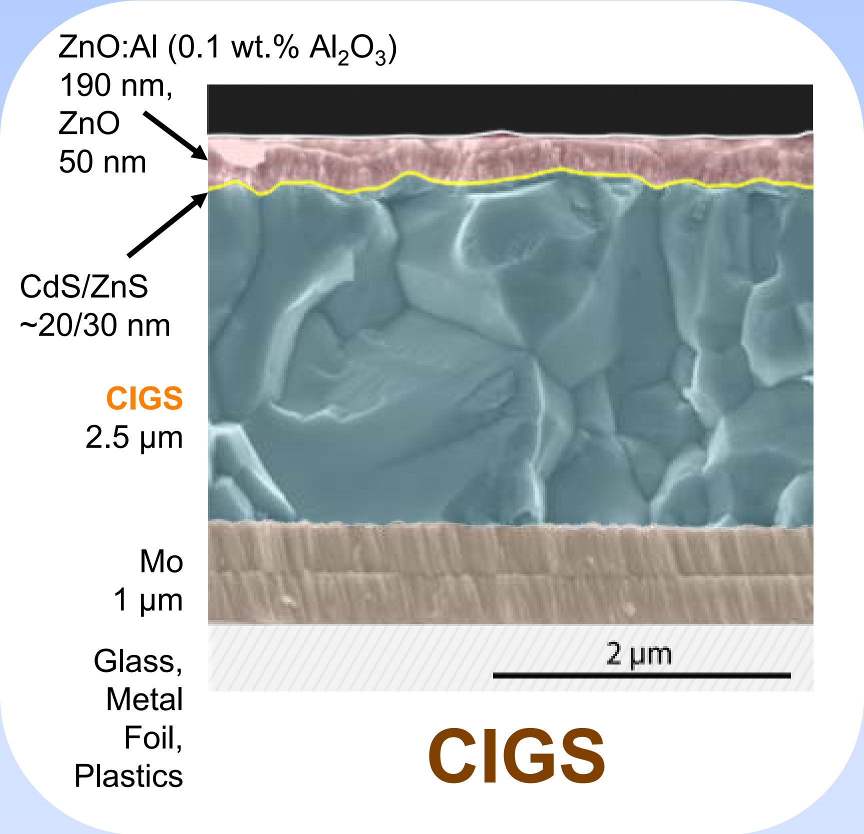
- CdS by chemical bath deposition
- 100 nm IZO, 120 nm ZnO:Al

Test:

0.1 wt.% Al_2O_3

- CdS/ZnS (~20/30 nm)
- 100 nm IZO, 120 nm ZnO:Al

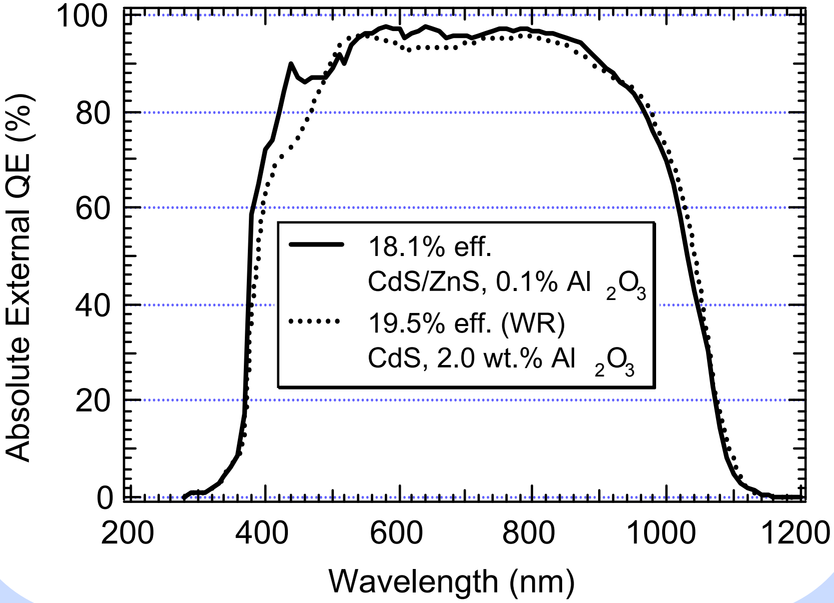




CIGS PV Device Studies - 2

- Efficiency, FF, V_{OC}, J_{SC} compare favorably with control sample
- QE: Difference at low wavelengths due to CdS vs. CdS/ZnS
- At higher wavelengths, QE of 0.1% Al_2O_3 cell rivals 19.5% WR cell

Comparing ZnO:Al doping levels on CIGS



Al_2O_3 Content (wt.%)	Treatment	Efficiency (%)	Fill Factor (%)	Open-curcuit voltage (mV)	Short-circuit current (mA/cm^2)
0.1	CdS/ZnS	18.1	76.2	671	35.4
2.0	CdS	18.1	79.1	666	34.4

Conclusions

- Lightly-doped ZnO (grown in H_2) can substitute for the standard 2.0 wt.% Al_2O_3
  - increased carrier mobility
  - increased near-IR transmittance
- Addition of H_2 enables best mobility and carrier concentration for ZnO:Al using room T deposition and increased tolerance for higher T
- In initial CIGS PV device studies:
  - Efficiency, FF, V_{OC}, J_{SC} compare favorably with control
  - QE comparable to former WR cell at higher wavelengths

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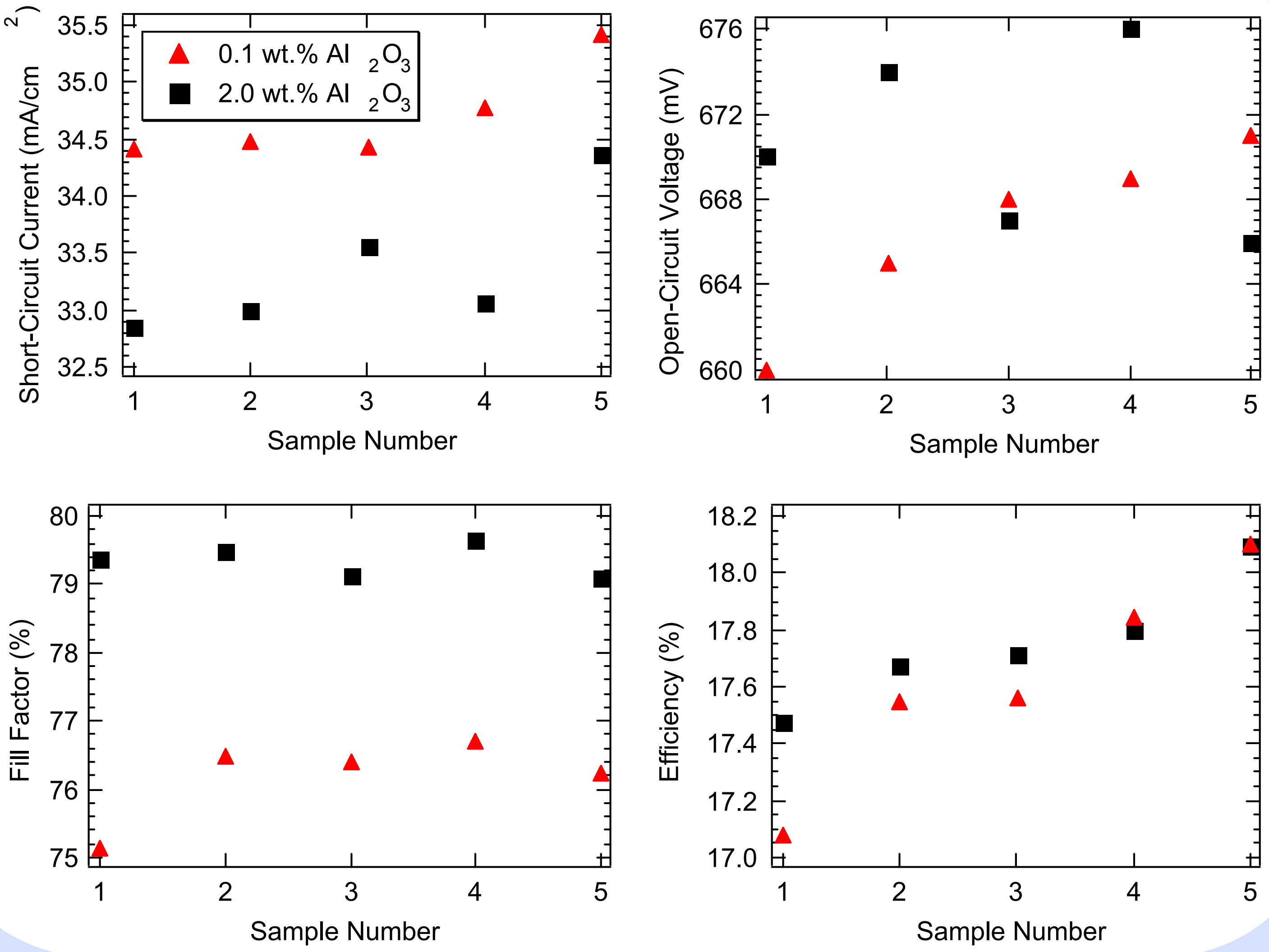
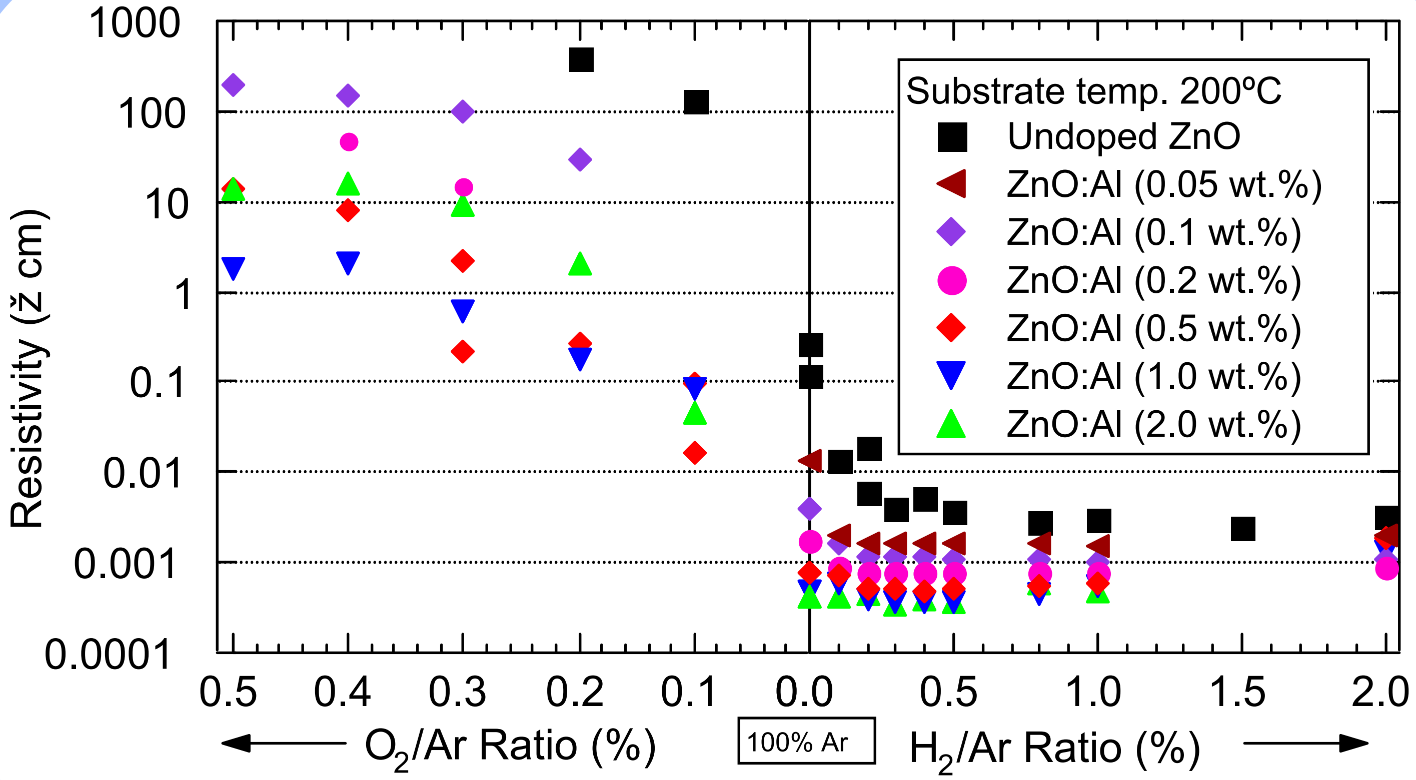
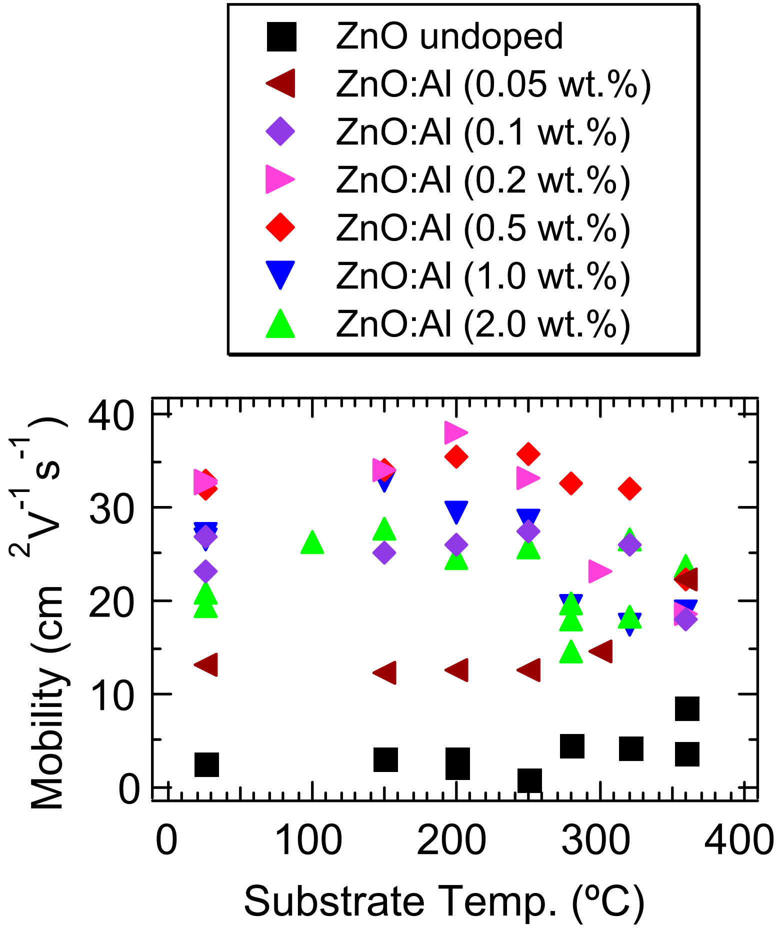
All CIGS PV Device Results

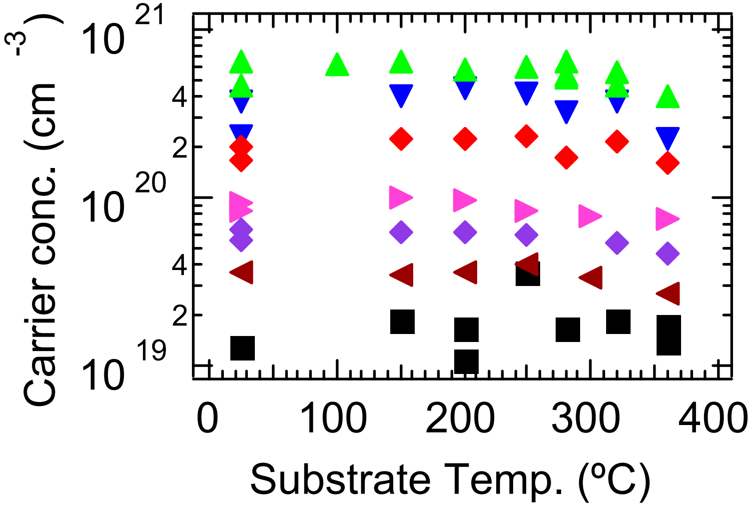


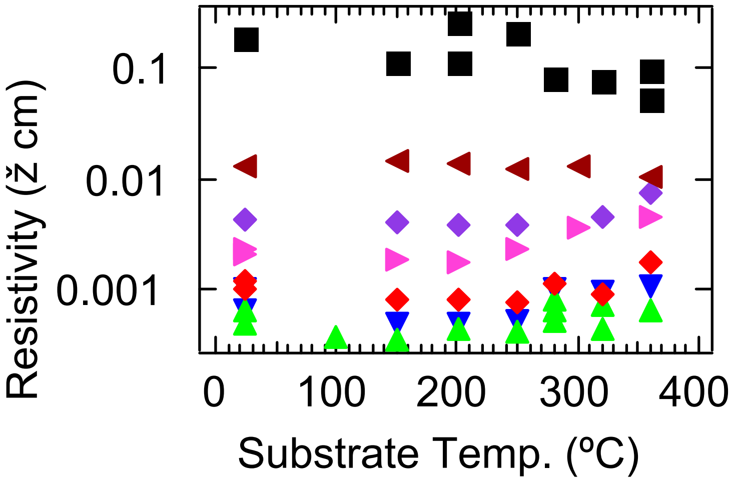
Resistivity vs. O_2/Ar and H_2/Ar Ratios



Electrical Properties vs. Substrate Temp.

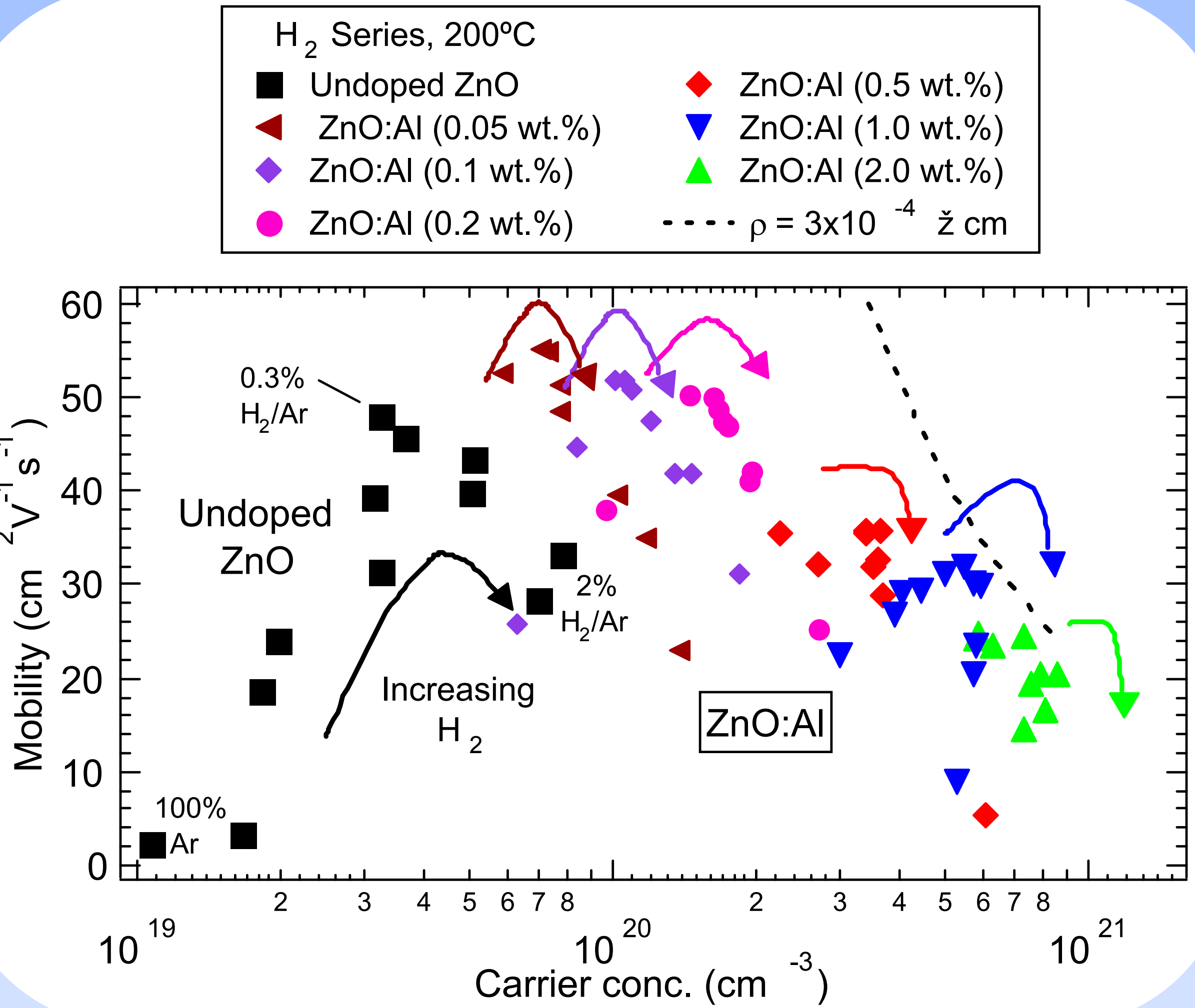






All films grown in 100% Ar

Mobility (μ) vs. Carrier Concentration (n)



Undoped ZnO

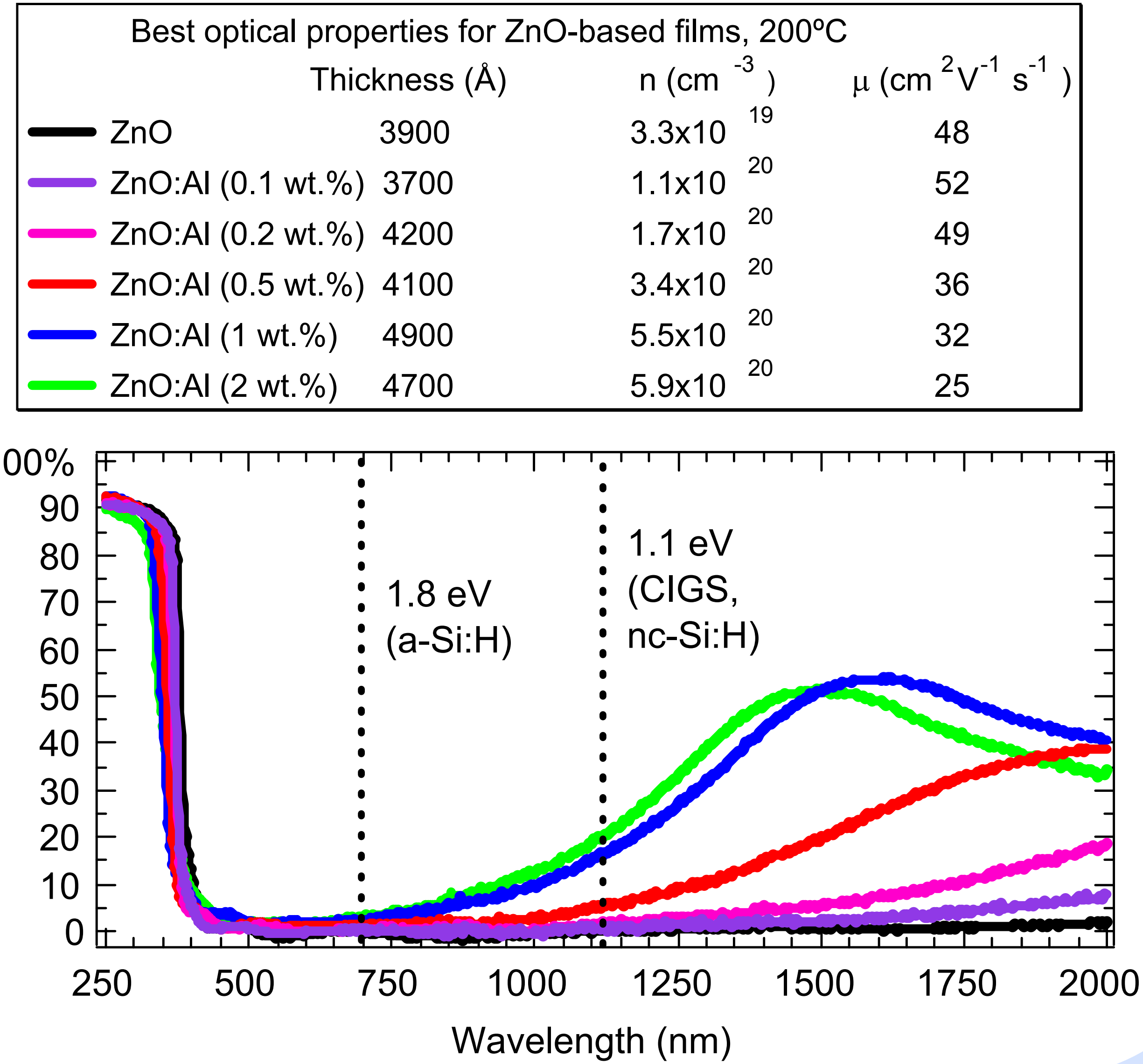
- Passivation of defects by H

ZnO:Al

- Activation of dopant with H
- Ionized impurity scattering

H_2: Filling sites (e.g. on grain boundaries) on which dopant atoms would not contribute carriers?

Absorptance vs. Wavelength

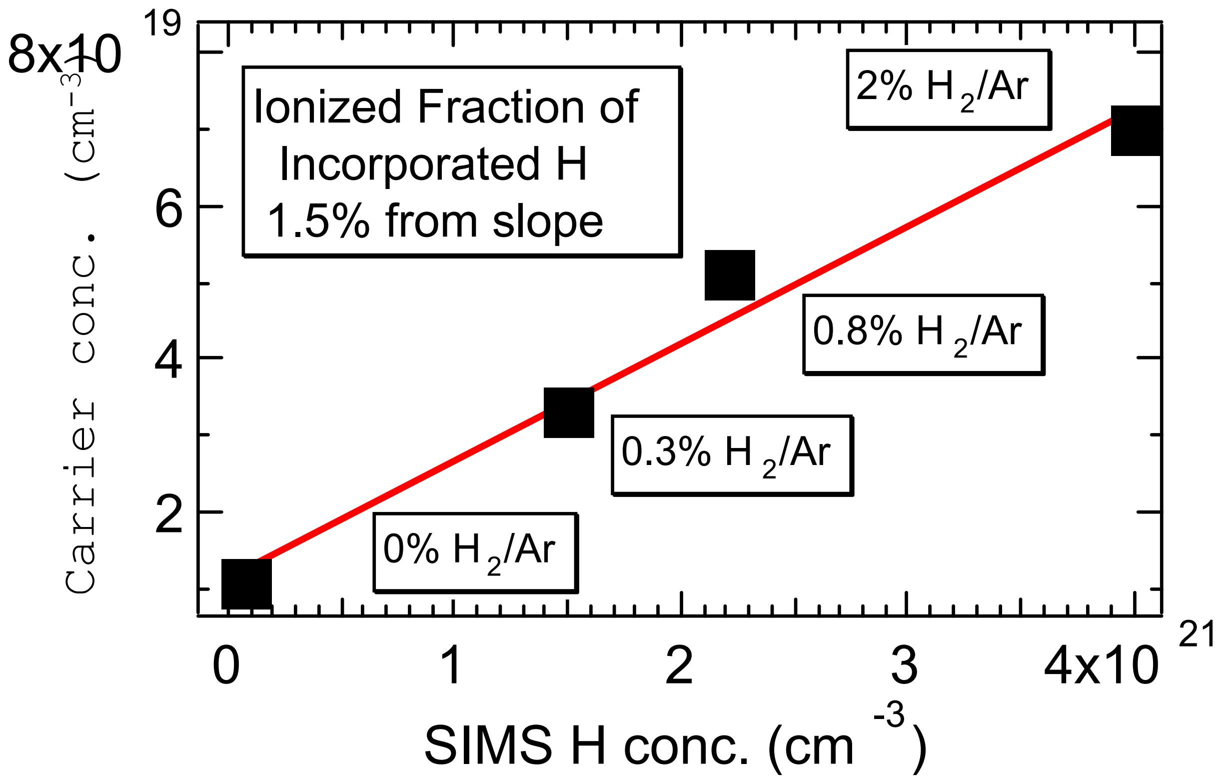


Best optical properties for ZnO-based films, 200ºC

		Thickness (Å)	n (cm^{-3})	μ ($cm^2 V^{-1} s^{-1}$)
▬	ZnO	3900	$3.3x10^{19}$	48
▬	ZnO:Al (0.1 wt.%)	3700	$1.1x10^{20}$	52
▬	ZnO:Al (0.2 wt.%)	4200	$1.7x10^{20}$	49
▬	ZnO:Al (0.5 wt.%)	4100	$3.4x10^{20}$	36
▬	ZnO:Al (1 wt.%)	4900	$5.5x10^{20}$	32
▬	ZnO:Al (2 wt.%)	4700	$5.9x10^{20}$	25

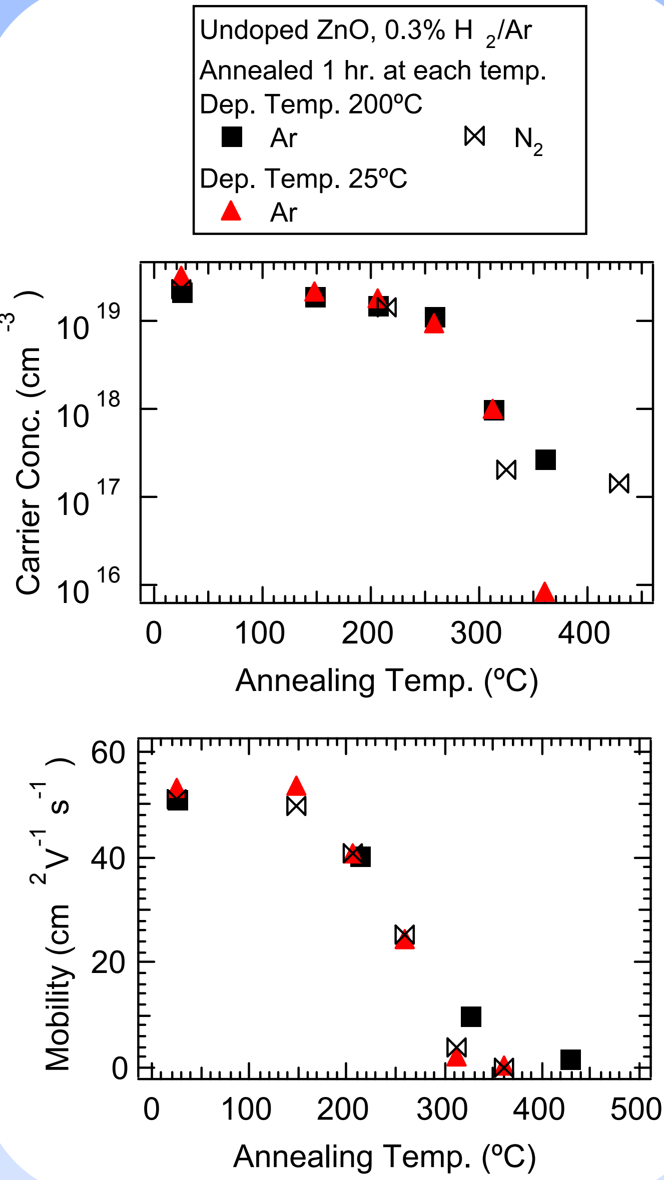
To what extent is H_2 incorporated in films?

- SIMS measurements show ~10^{21} cm^{-3} H conc.
- But carrier conc. is ~10^{19} cm^{-3}, so most H not ionized



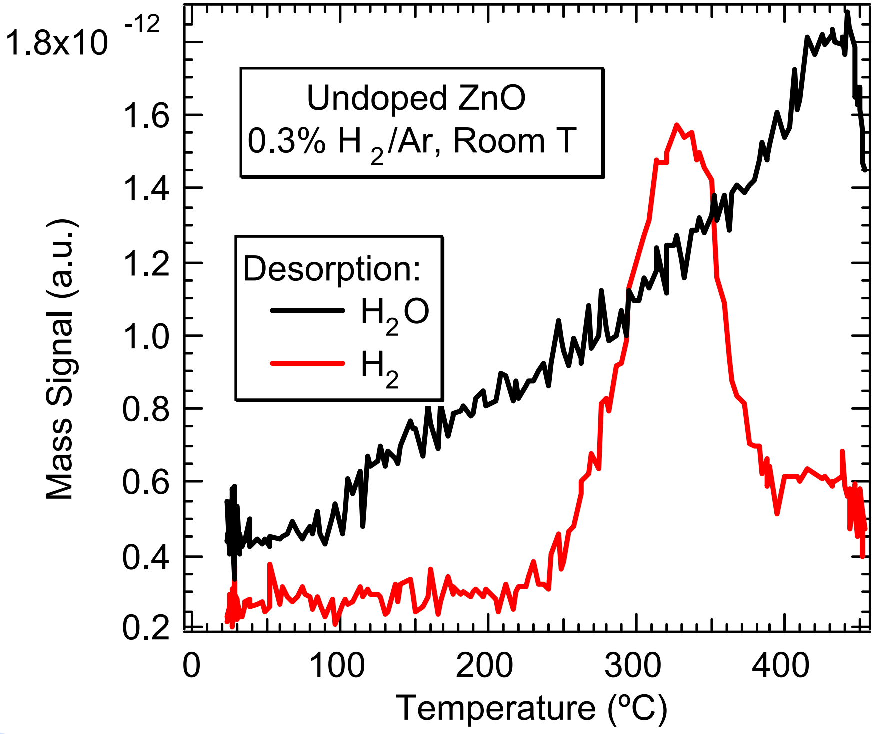
SIMS measurements by Matthew R. Young, NREL

At what T is H_2 removed from ZnO?



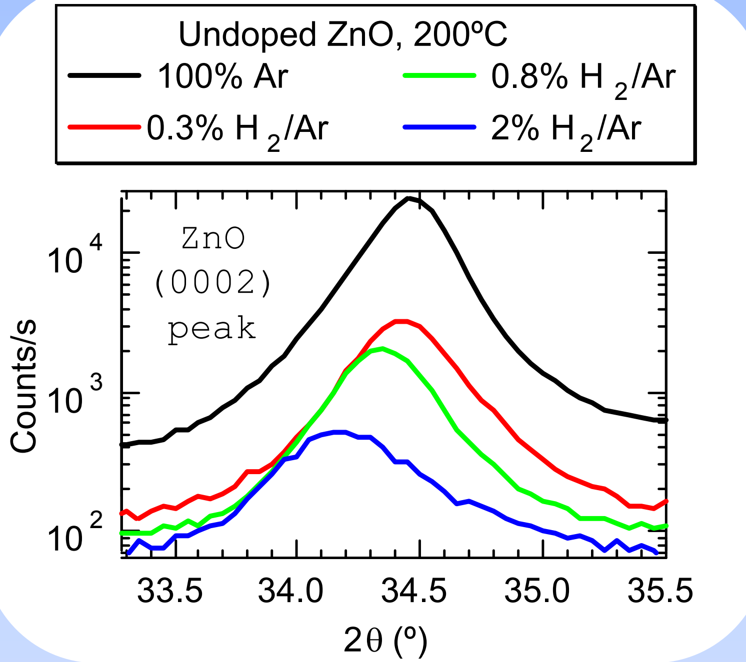
- Decrease in carrier concentration and mobility appears near temp. at which desorption occurs

Temperature-Programmed Desorption



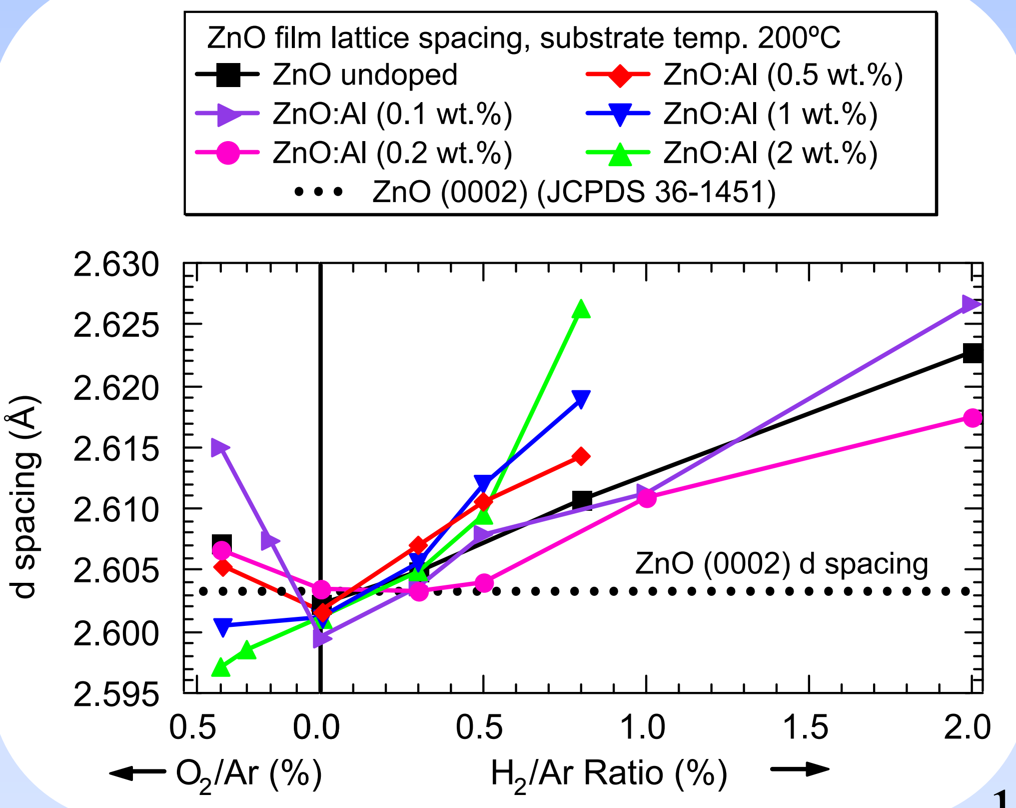
Measurement performed by Anne Dillon, NREL

Structure - H_2 and Thickness effects



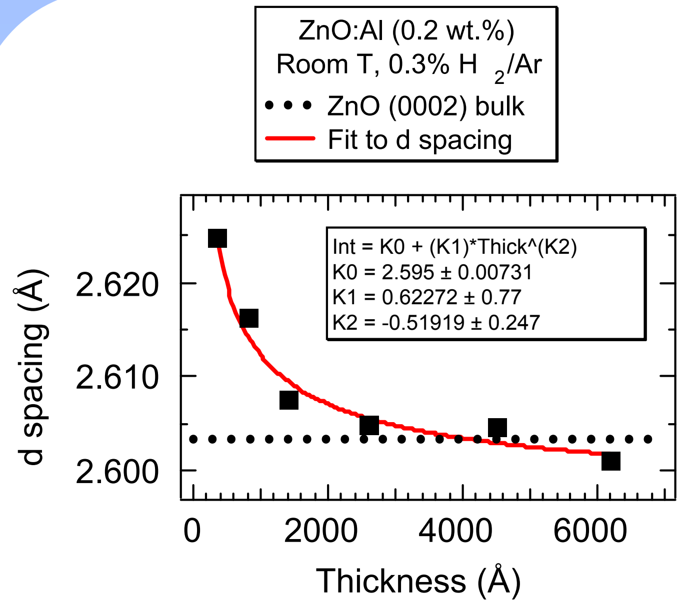
- Peak shifts to lower angle and decreases in intensity with H_2/Ar
- But film thickness also decreases by up to 50% with growth in H

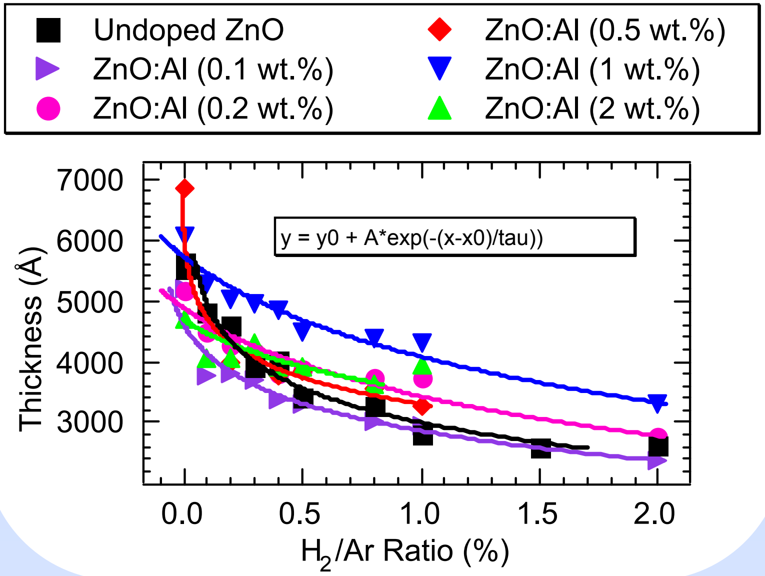
- Is change in d spacing due to H_2 or thickness?
- To what extent is H_2 incorporated into films?

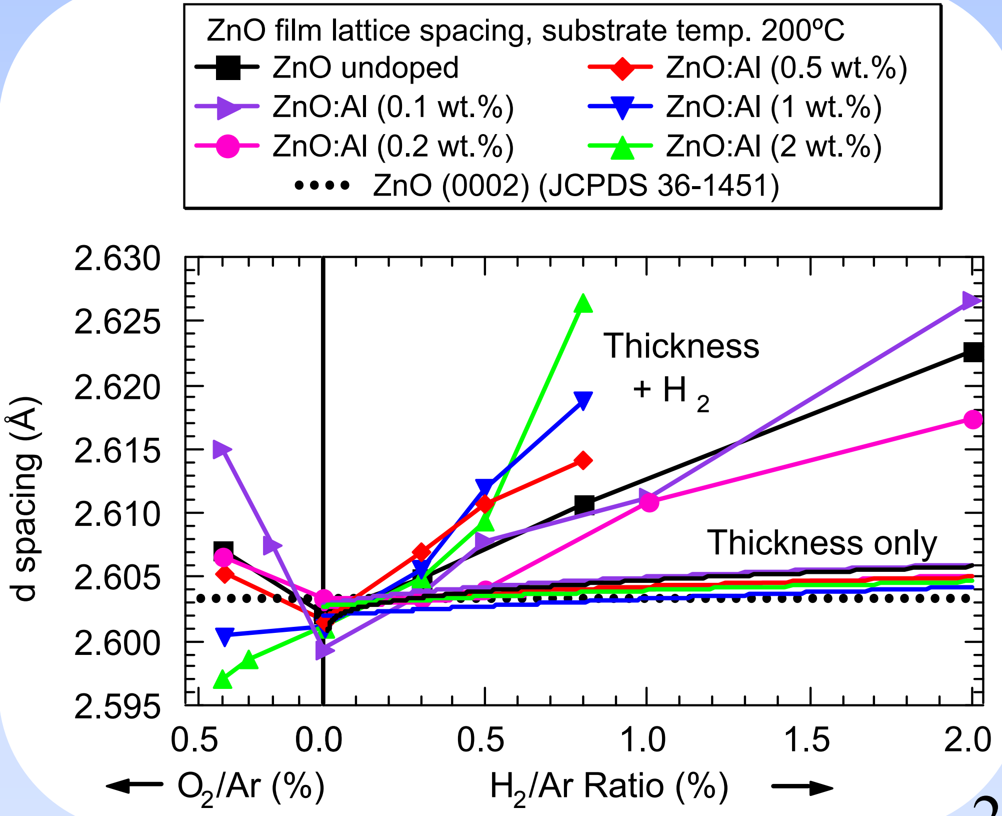


Separating H_2 and Thickness Effects

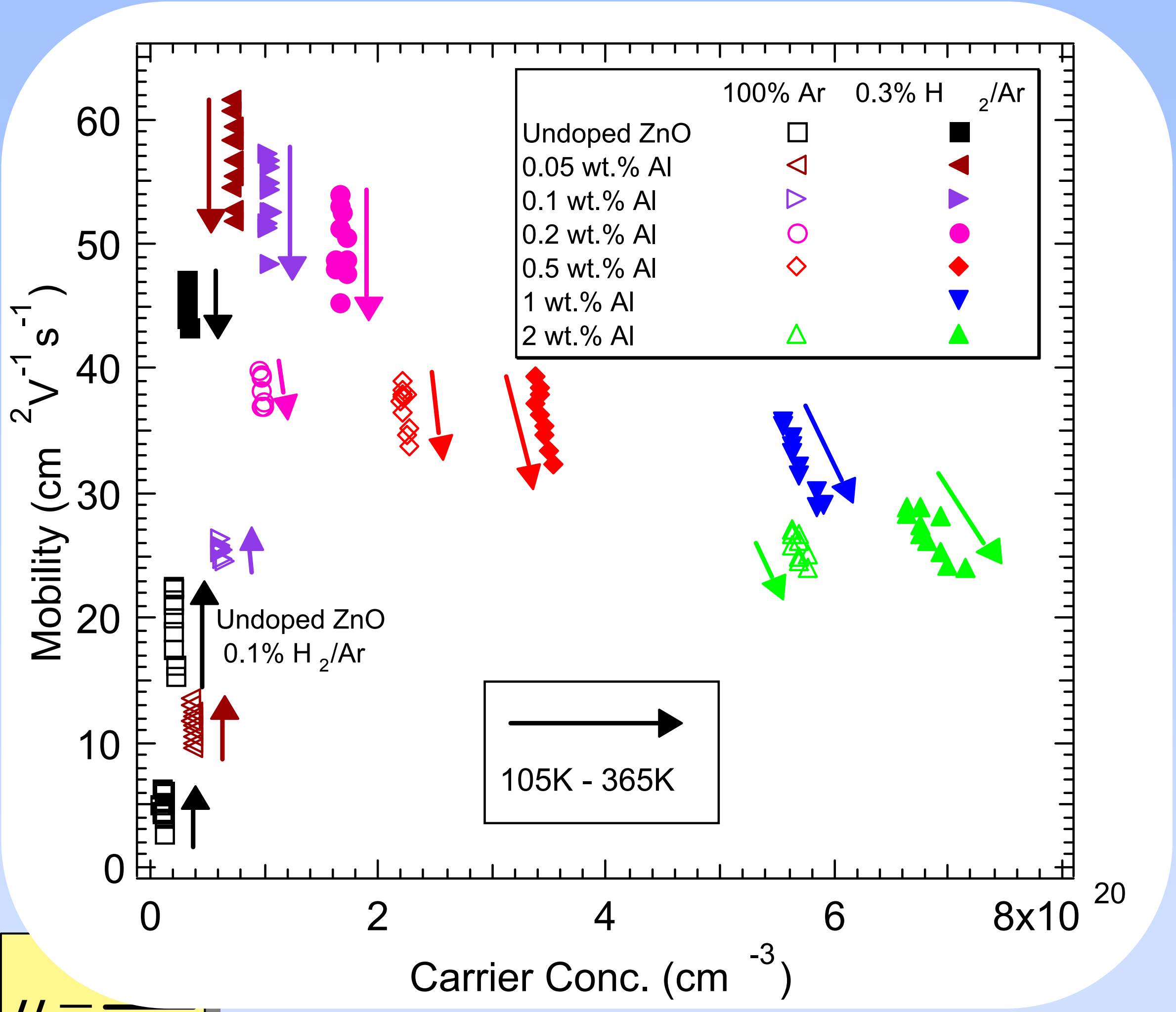
- Empirical fit of d spacing vs. thickness for fixed Al and H_2 amounts
- Fit of H_2 vs. thickness for all Al amounts
- H_2 effect dominates







Scattering Mechanisms Using T-dep. Hall



Undoped ZnO

0.1% H_2/Ar

- Temp. activation ⇒barrier (dangling bonds?)

0.3% H_2/Ar

- Phonon scattering
- Passivation of dangling bonds at grain boundaries

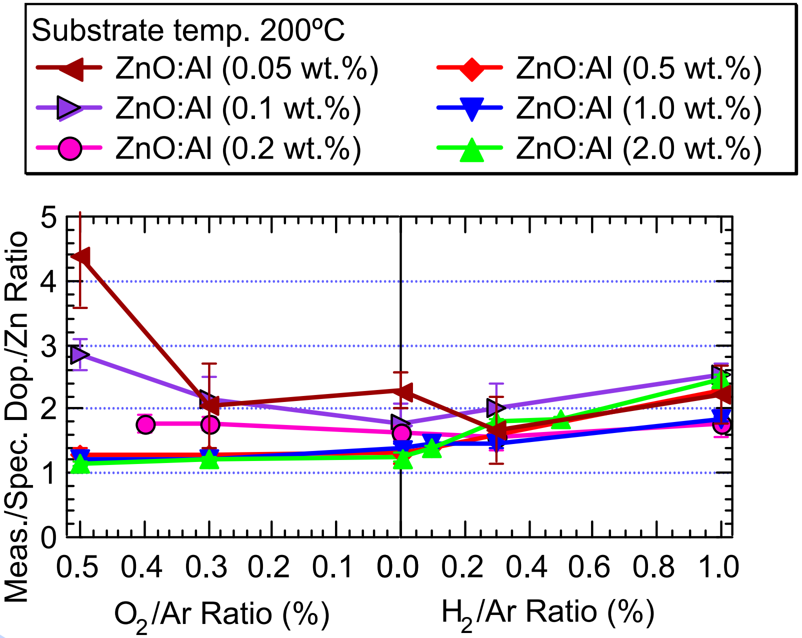
ZnO:Al

- Increasing ionized impurity scattering with Al dopant

$$\mu = \frac{\quad}{m^*}$$

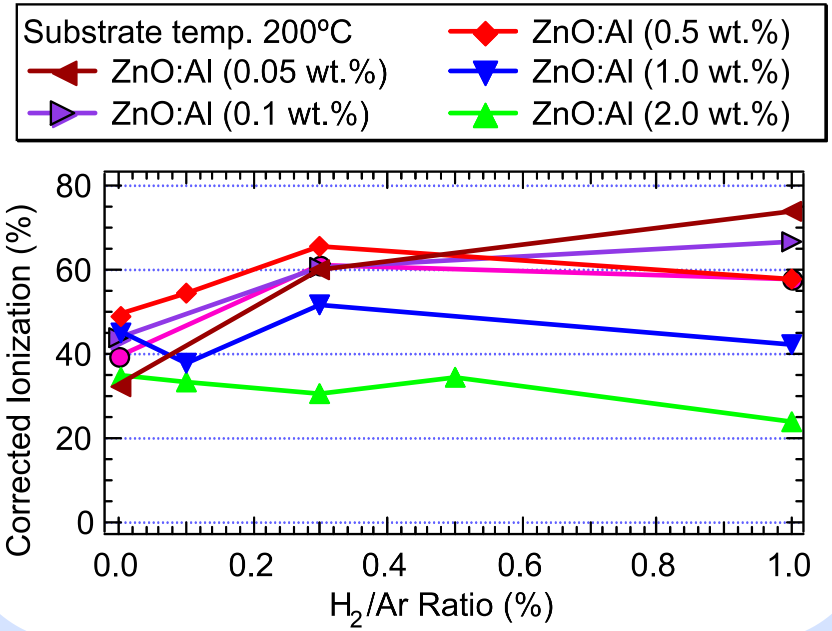
$$\frac{1}{\tau} = \frac{1}{\tau_{ionized}} + \frac{1}{\tau_{neutral}} + \frac{1}{\tau_{phonon}} + \ldots$$

Dopant Ionization - EPMA



- Mo-doped films contain near the amount of dopant specified
- Al-doped films all contain greater amts. of Al

$$\text{Ionization \%} = \frac{n_{\text{Doped}} - n_{\text{Undoped ZnO}}}{n_{\text{EPMA}}}$$

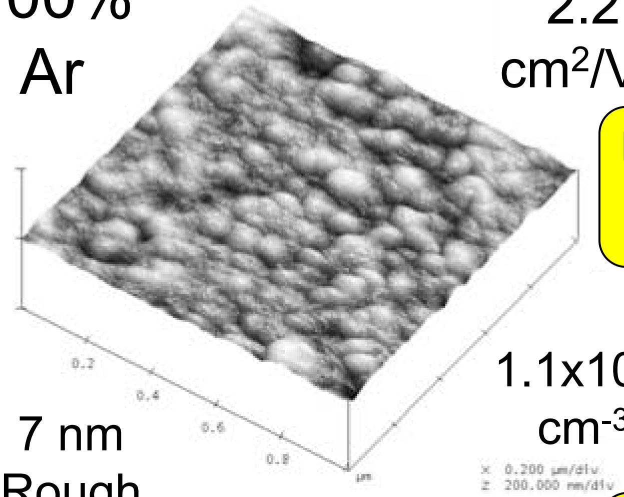


- Limited H_2 aids ionization
- Ionization decreases with Al level
- Mo has poorest ionization

Measurements performed by Bobby To, NREL

100% Ar

2.2 cm^2/Vs



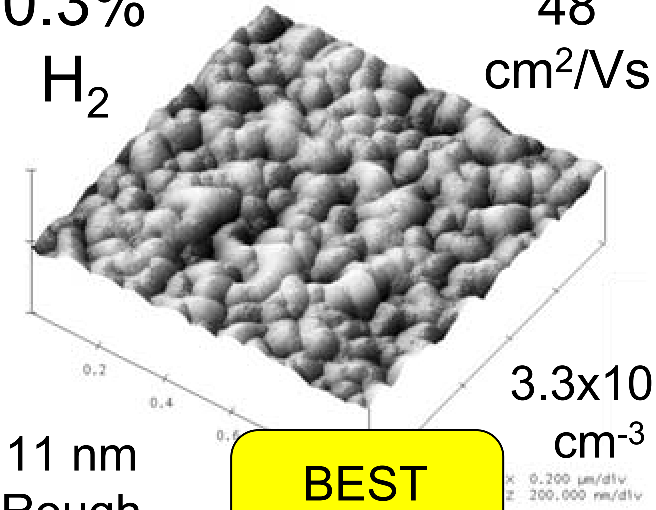
$1.1x10^{19}$ cm^{-3}

7 nm Rough

Undoped ZnO

0.3% H_2

48 cm^2/Vs



$3.3x10^{19}$ cm^{-3}

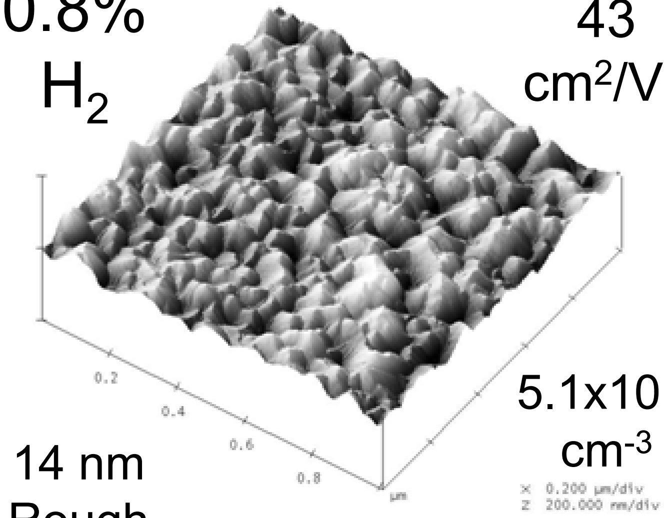
11 nm Rough

BEST MOBILITY

1 µm on a side

0.8% H_2

43 cm^2/Vs

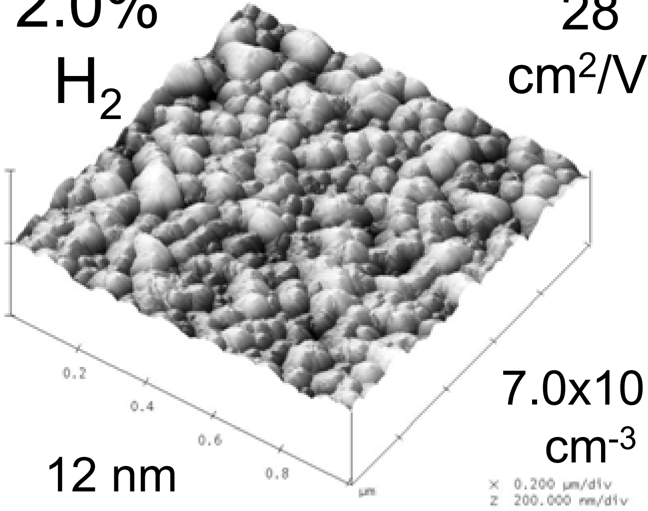


$5.1x10^{19}$ cm^{-3}

14 nm Rough

2.0% H_2

28 cm^2/Vs



$7.0x10^{19}$ cm^{-3}

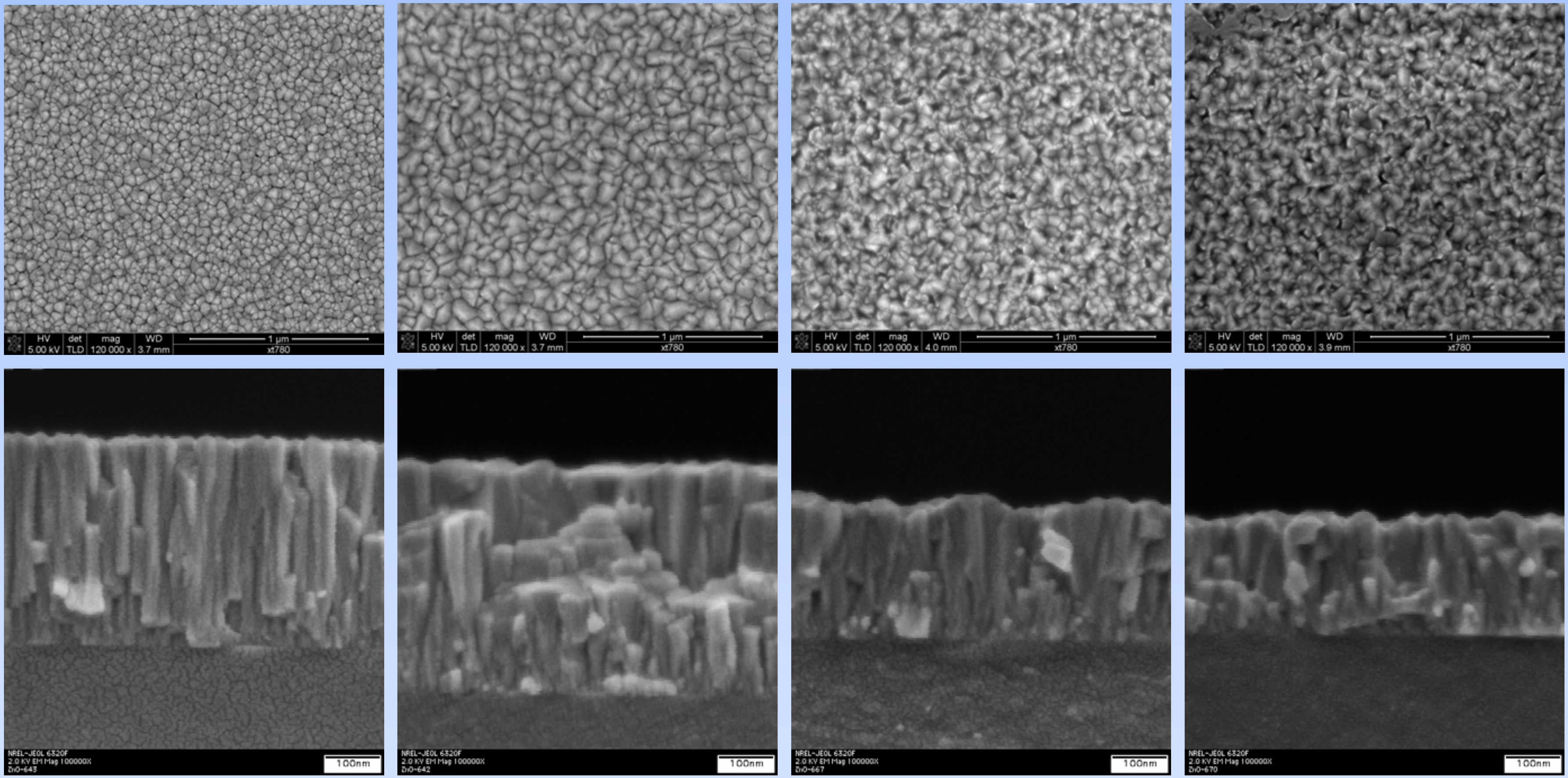
12 nm Rough

AFM measurements by Bobby To, NREL

Film Structure from SEM

0.1% Al_2O_3
200ºC

0.3% O_2/Ar | 100% Ar | 0.4% H_2/Ar | 1.0% H_2/Ar



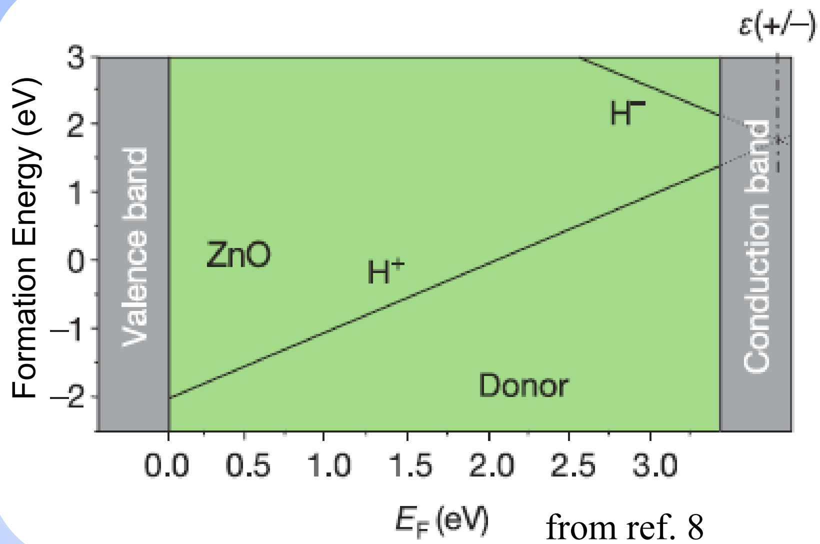
Performed by Bobby To, NREL

Scales
Top: 2.1 µm wide
Bottom: 0.73 µm wide

Increasing roughness and faceting →
Increasing lateral crystallite growth
Does lateral growth improve electrical properties?

Native Defects: Why is Undoped ZnO n-type?

- Oxygen vacancies?[1-3]
  - High formation energy, deep donor[4]
- Zn interstitials?[5]
  - High formation energy, high diffusivity[4]
- Hydrogen as dopant (bonded to O)
  - H interstitial[6]
  - H_2 in Zn vacancy[7]
  - H always a donor in ZnO[8-11]



from ref. 8

[1] G.D. Mahan, J. Appl. Phys. **54**, 3825 (1983).
[2] E. Ziegler *et. al.*, Phys. Status Solidi A **66**, 635 (1981).
[3] A.F. Kohan *et. al.*, Phys. Rev. B **61**, 15019 (2000).
[4] A. Janotti and C.G. Van de Walle, J. Crys. Growth **287**, 58 (2006).
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[6] C.G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).
[7] E. V. Lavrov *et. al.*, Phys. Rev. B **66**, 165205 (2002).
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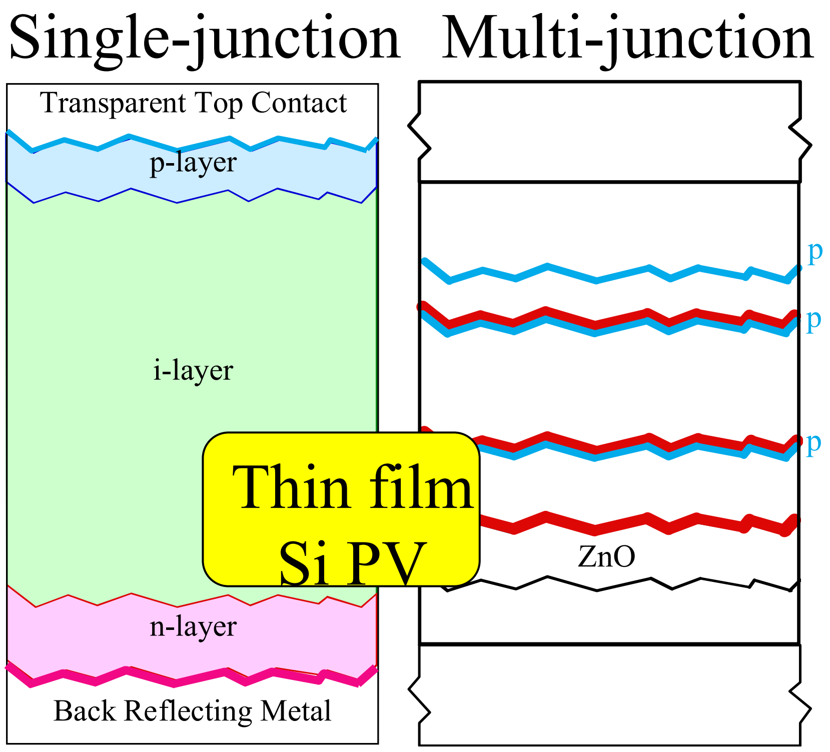
[9] C.G. Van de Walle, Phys. Stat. Sol. B **235**, 89 (2003).
[10] Ç. Kiliç and A. Zunger, Appl. Phys. Lett. **81**, 73 (2002).
[11] A. Janotti and C.G. Van de Walle, Nature Materials **6**, 44 (2007).

Benefits of ZnO TCO

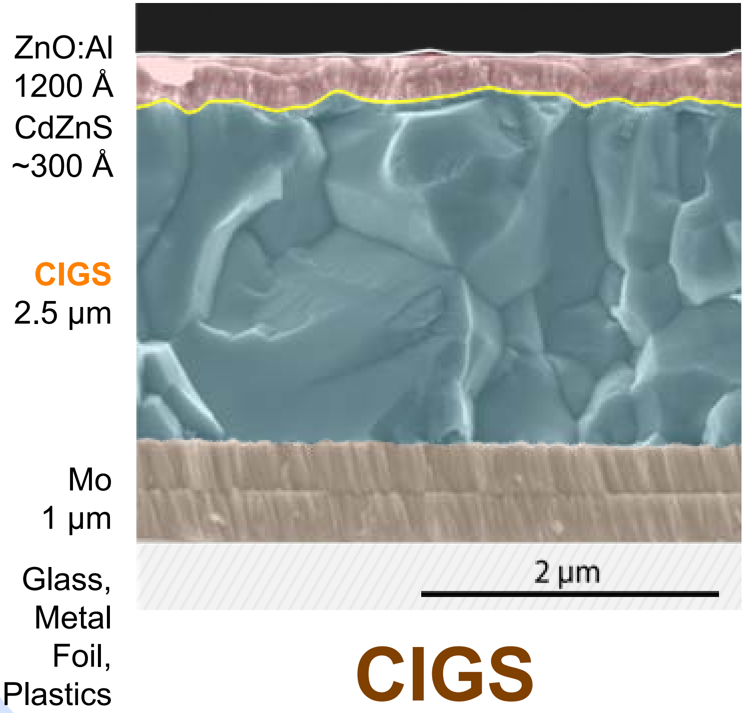
- May be less expensive than comparable materials (e.g. ITO)
- No adverse effects from H_2-rich plasma
- High transparency in visible and near-IR



Single-junction Multi-junction

Thin film Si PV

Brent Nelson, NREL



CIGS

R. Noufi, NREL