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

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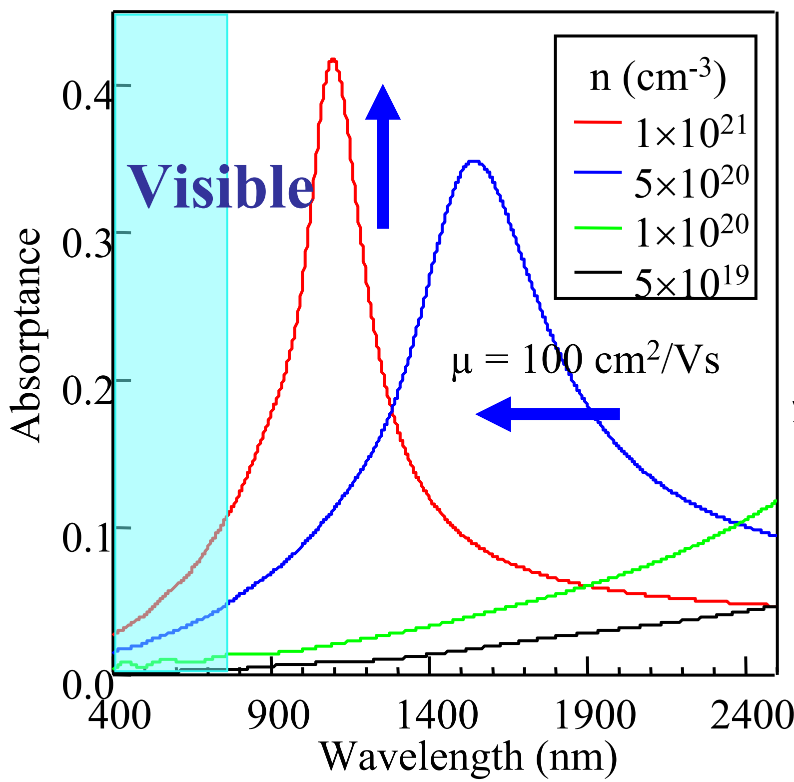
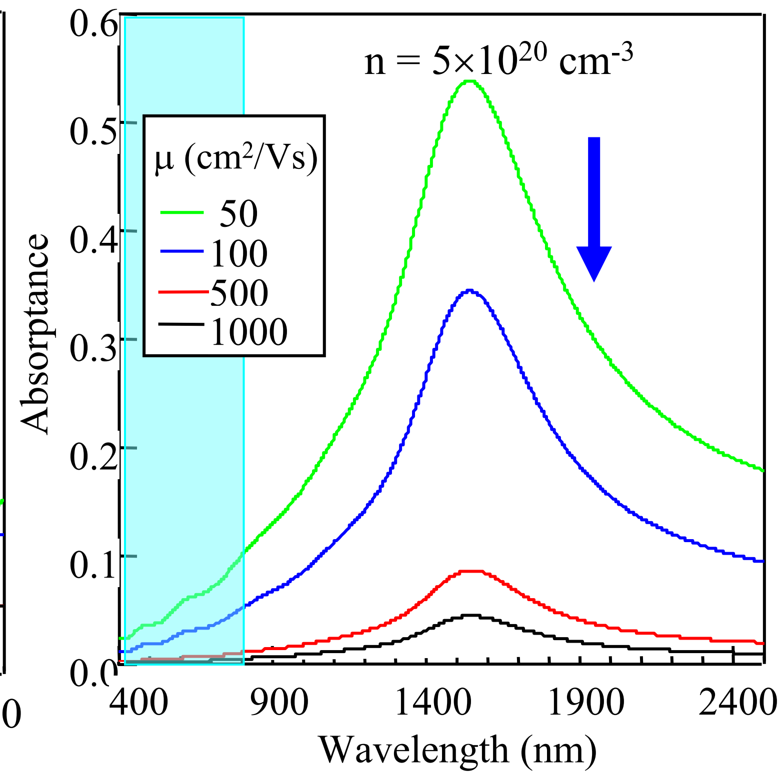
Modeled TCO Absorptance

Varying carrier conc.



Varying mobility



A=1-T-R $\sigma = qn\mu$

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

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

Target cooling water

RF power

Sputter gun

Fully oxidized planar 3" target

Vacuum chamber

Gas inlets

Ar
H_2
O_2

Corning 7059 or 1737 Substrate

ion gauge

Rough pump

Cryogenic pump

Electrical Data - Ambient Studies

Carrier Conc. (cm^{-3})

10^{21}
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}

Mobility ($cm^2 V^{-1} s^{-1}$)

60
50
40
30
20
10
0

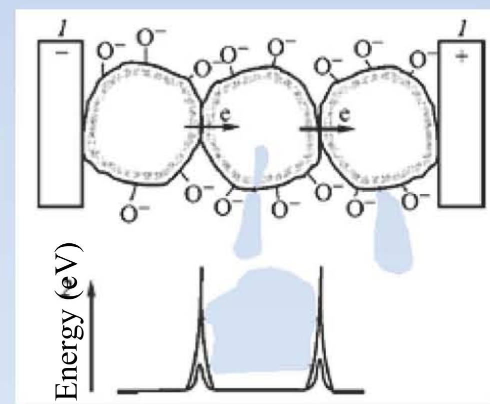
0.5 0.4 0.3 0.2 0.1 0.0 0.5 1.0 1.5 2.0

O_2/Ar Ratio (%) 100% Ar H_2/Ar Ratio (%)

All depositions at 200ºC

Undoped ZnO
ZnO:Al (0.05 wt.%)
ZnO:Al (0.1 wt.%)
ZnO:Al (0.2 wt.%)
ZnO:Al (0.5 wt.%)
ZnO:Al (1.0 wt.%)
ZnO:Al (2.0 wt.%)

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

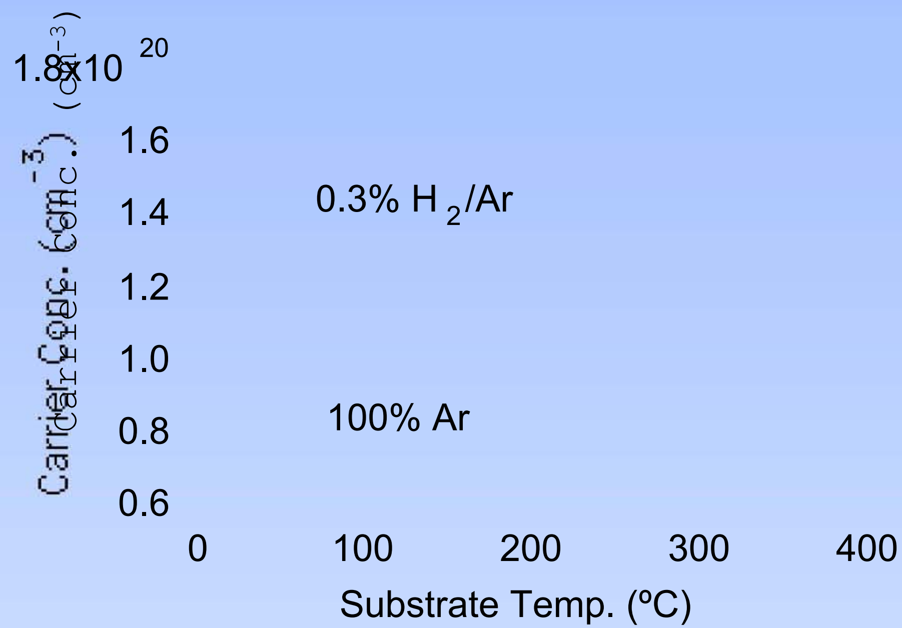


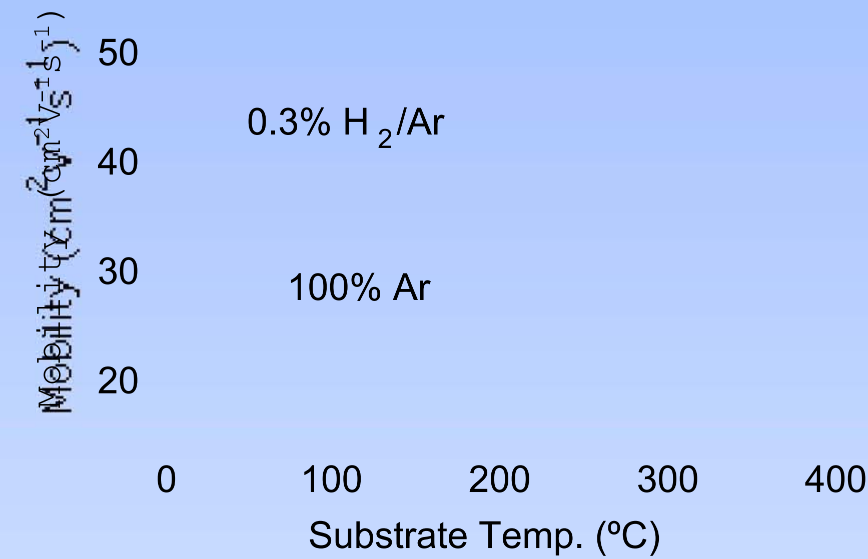
Position

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

$m_c^* \sim 0.3 m_e$

$E_{gap} + \Delta E_{BM}$ E_F

E_{gap}

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}

T (%), R (%)
100% 90 80 70 60 50 40 30 20 10 0
%T
%R
1.8 eV (a-Si:H)
1.1 eV (CIGS, nc-Si:H)
250 500 750 1000 1250 1500 1750 2000
Wavelength (nm)

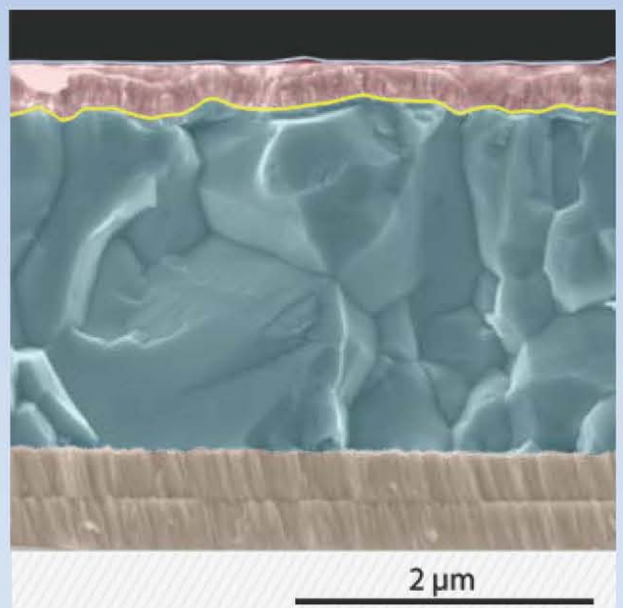
Transmittance (%)
80% 60 40 20 0
320 340 360 380
Wavelength (nm)

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

CIGS PV Device Studies

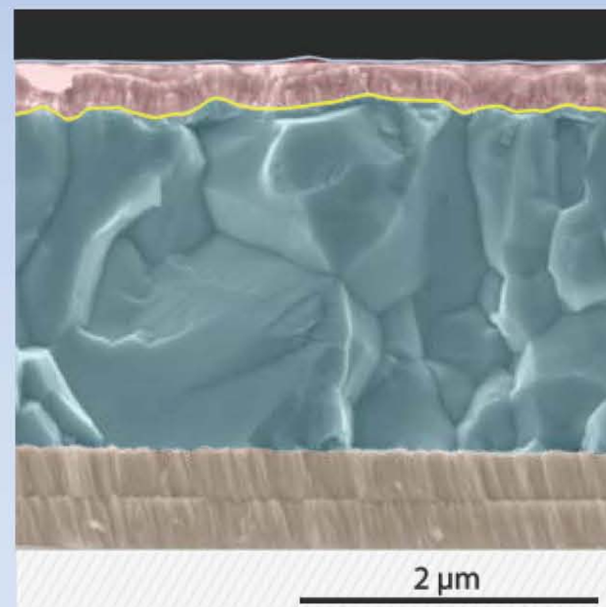
Control:

- 2.0 wt.% Al_2O_3
  - CdS by chemical bath deposition
  - 100 nm IZO, 120 nm ZnO:Al



Test:

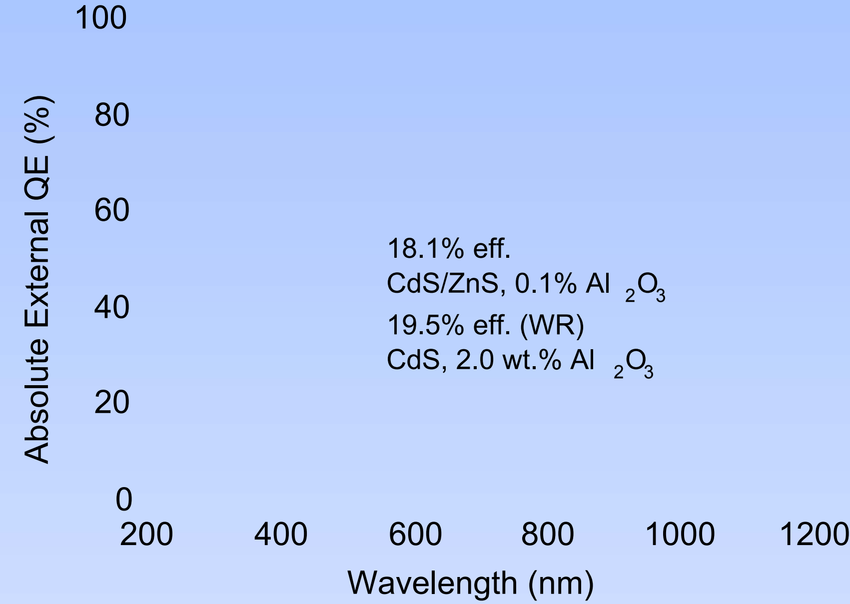
- 0.1 wt.% Al_2O_3
  - CdS/ZnS (~20/30 nm)
  - 100 nm IZO, 120 nm ZnO:Al



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

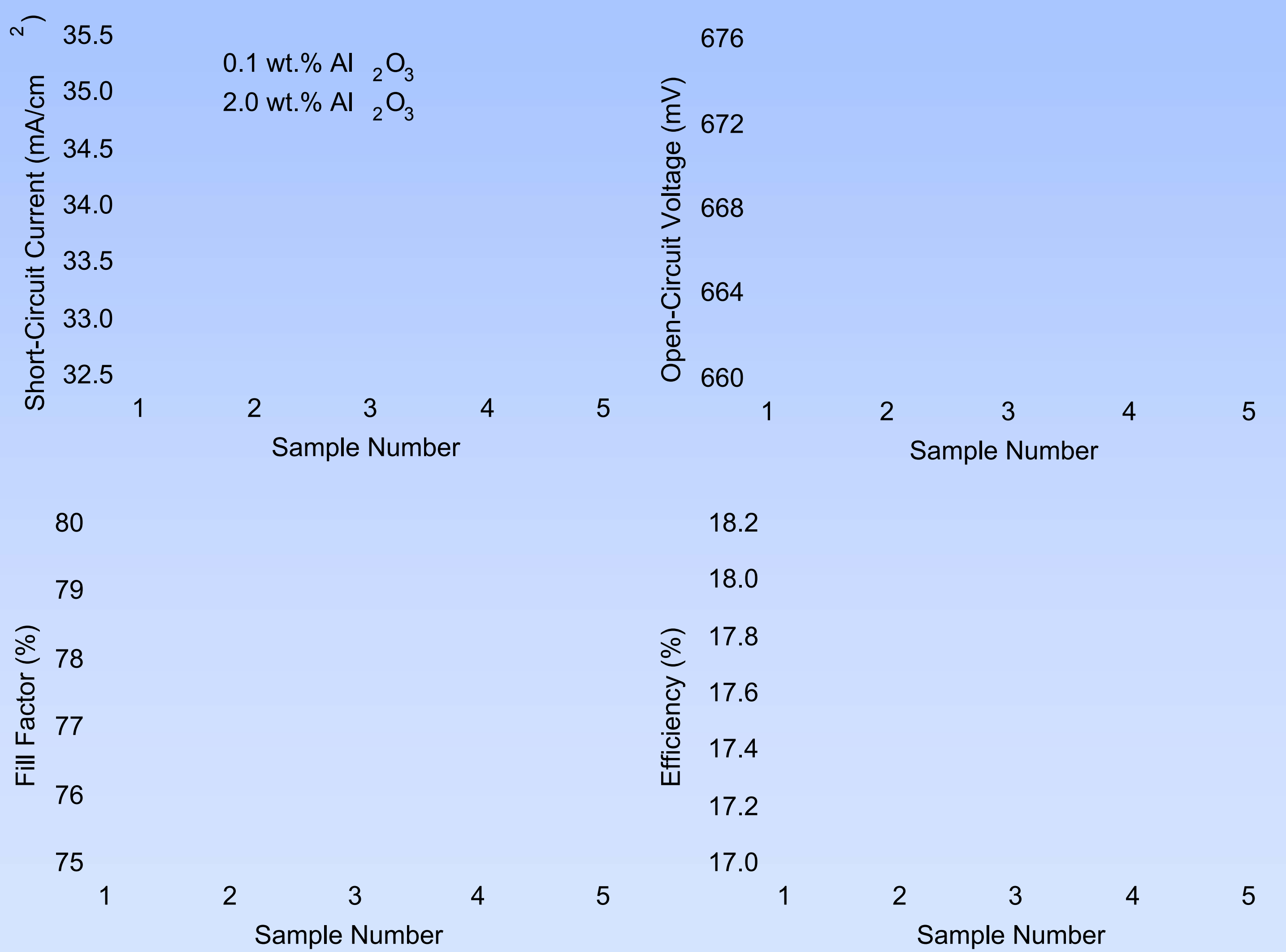


Al_2O_3 Content (wt.%)	Treatment	Efficiency (%)	Fill Factor (%)	Open-curcuit voltage (mV)	Short-circuit current (mA/cm^2)
0.1	CdS/ZnS	18.1	76.2	671	35.4
2.0	CdS	18.1	79.1	666	34.4

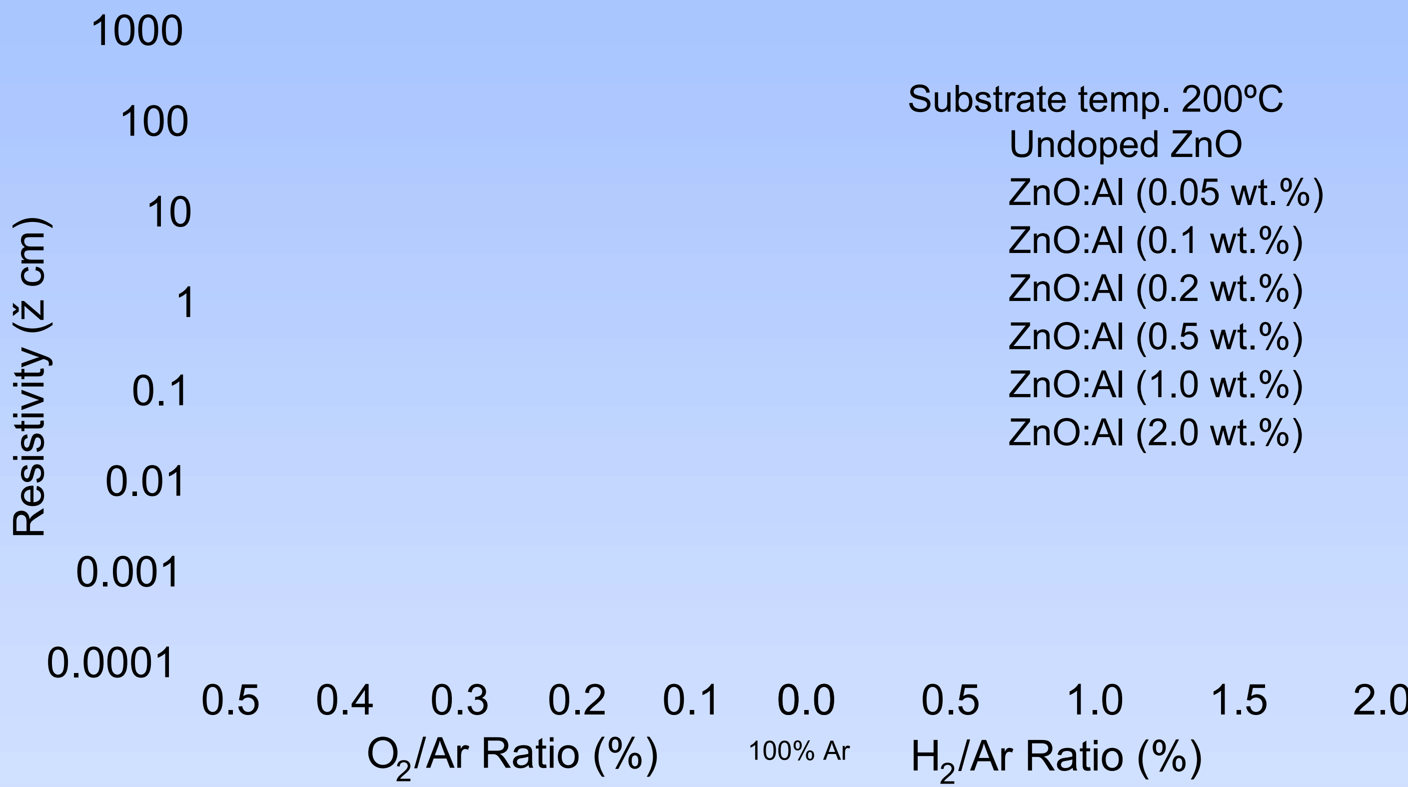
Conclusions

- 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

All CIGS PV Device Results



Resistivity vs. O_2/Ar and H_2/Ar Ratios



Electrical Properties vs. Substrate Temp.

ZnO undoped
ZnO:Al (0.05 wt.%)
ZnO:Al (0.1 wt.%)
ZnO:Al (0.2 wt.%)
ZnO:Al (0.5 wt.%)
ZnO:Al (1.0 wt.%)
ZnO:Al (2.0 wt.%)

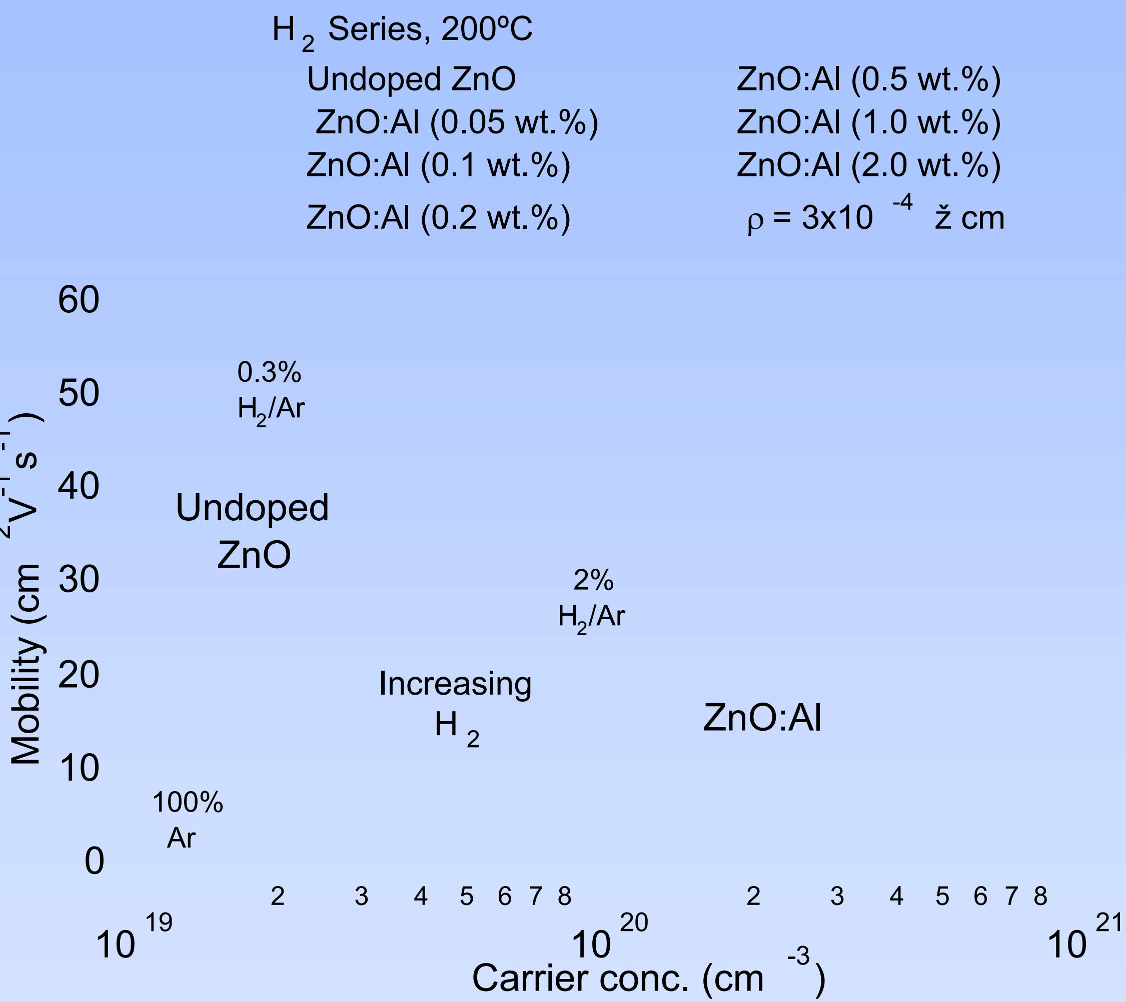
Carrier conc. (cm^{-3})
10^{21}
4
2
10^{20}
4
2
10^{19}
0 100 200 300 400
Substrate Temp. (ºC)

Mobility ($cm^2V^{-1}s^{-1}$)
40
30
20
10
0
0 100 200 300 400
Substrate Temp. (ºC)

Resistivity (ž cm)
0.1
0.01
0.001
0 100 200 300 400
Substrate Temp. (ºC)

All films grown in 100% Ar

Mobility (μ) vs. Carrier Concentration (n)



Undoped ZnO

- Passivation of defects by H

ZnO:Al

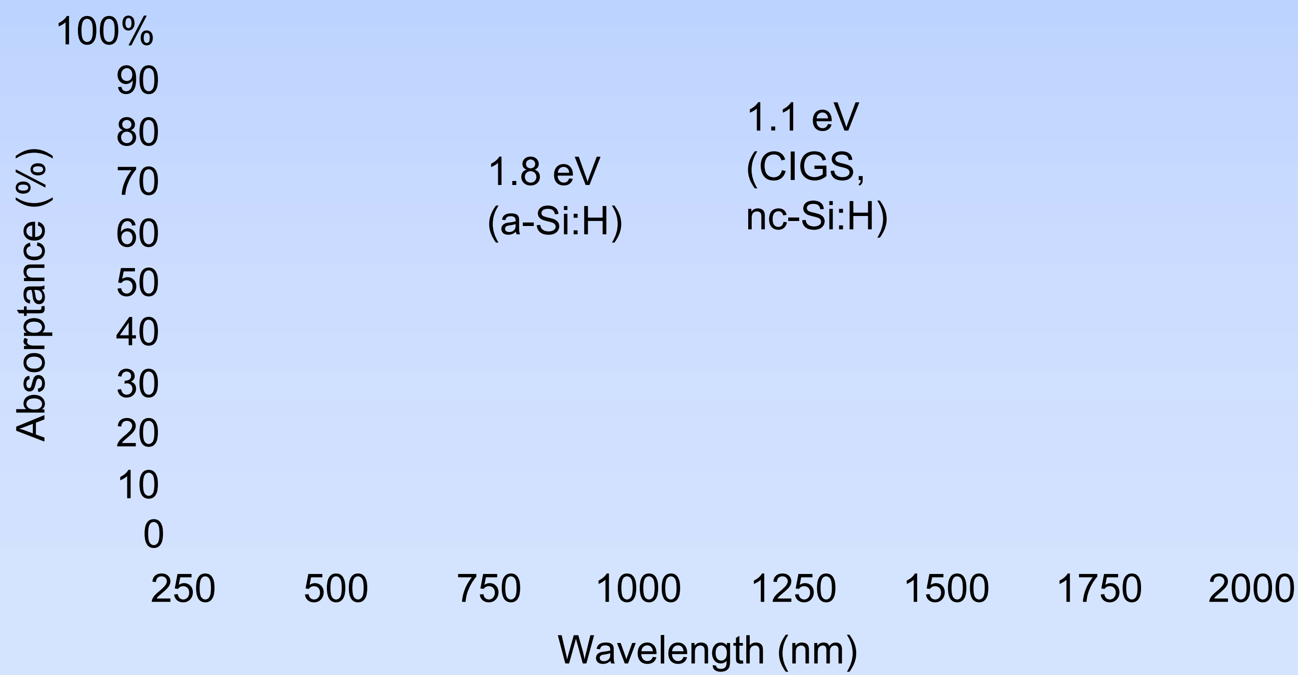
- Activation of dopant with H
- Ionized impurity scattering

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

Absorptance vs. Wavelength

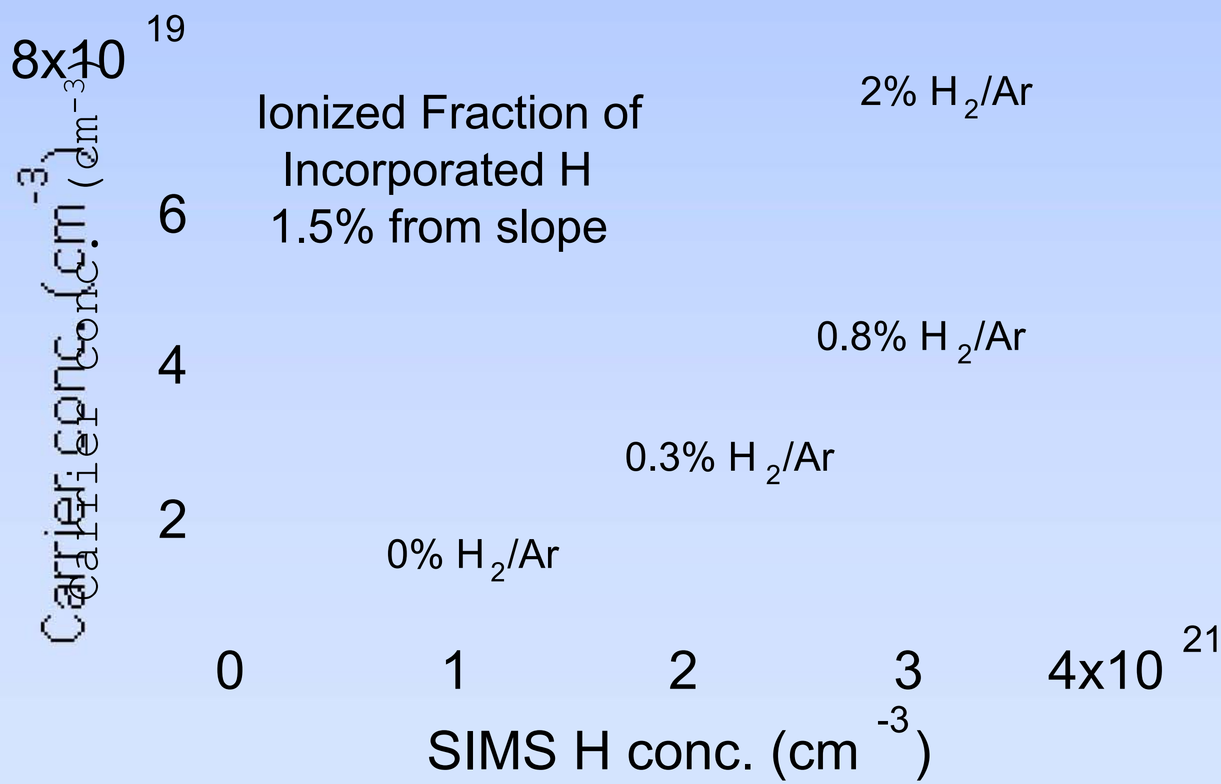
Best optical properties for ZnO-based films, 200ºC

	Thickness (Å)	n (cm^{-3})	μ ($cm^2V^{-1}s^{-1}$)
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



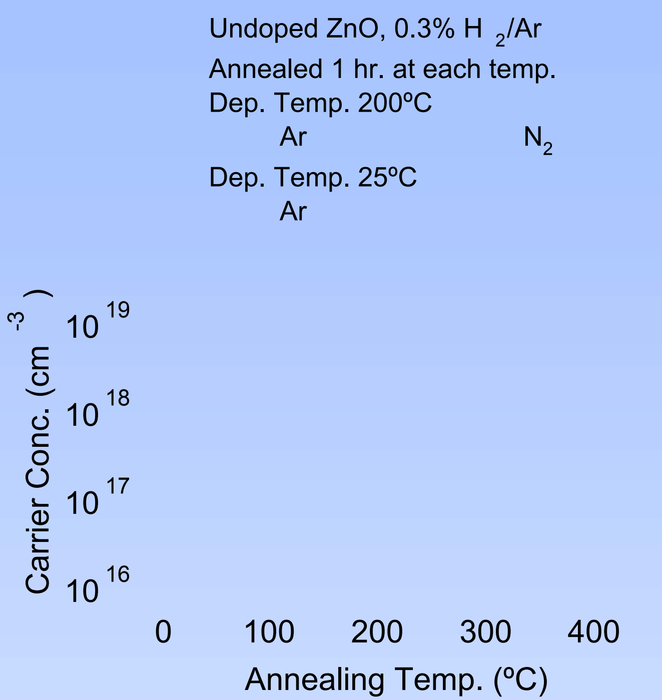
To what extent is H_2 incorporated in films?

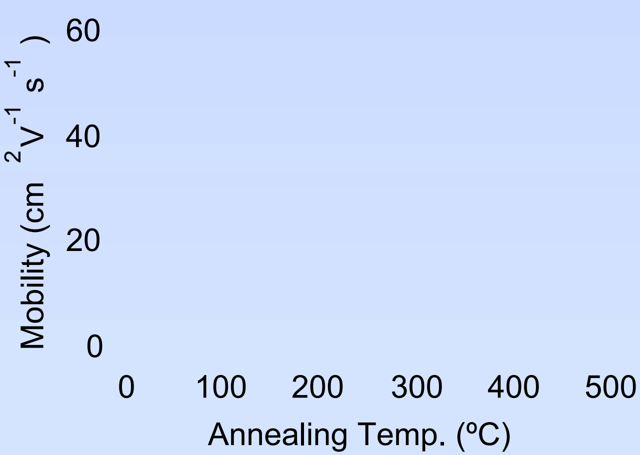
- SIMS measurements show ~10^{21} cm^{-3} H conc.
- But carrier conc. is ~10^{19} cm^{-3}, so most H not ionized



SIMS measurements by Matthew R. Young, NREL

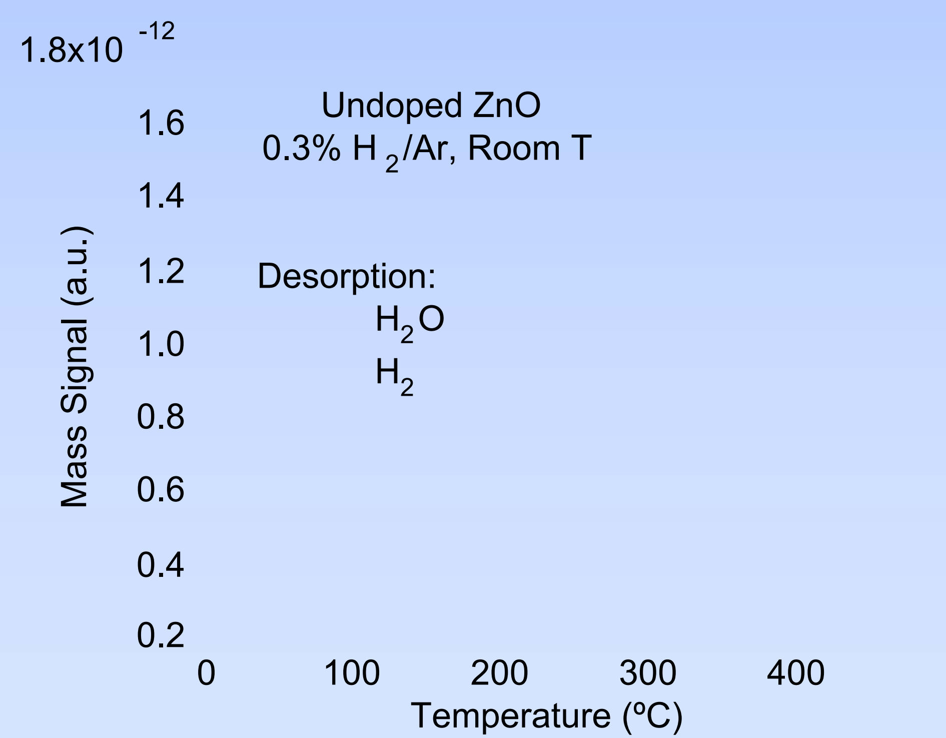
At what T is H_2 removed from ZnO?





- 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

Undoped ZnO, 200ºC

100% Ar

0.3% H_2/Ar

0.8% H_2/Ar

2% H_2/Ar

ZnO (0002) peak

Counts/s

10^4

10^3

10^2

33.5 34.0 34.5 35.0 35.5

2θ (º)

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

- 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_2

ZnO film lattice spacing, substrate temp. 200ºC

ZnO undoped

ZnO:Al (0.1 wt.%)

ZnO:Al (0.2 wt.%)

ZnO:Al (0.5 wt.%)

ZnO:Al (1 wt.%)

ZnO:Al (2 wt.%)

ZnO (0002) (JCPDS 36-1451)

d spacing (Å)

2.630 2.625 2.620 2.615 2.610 2.605 2.600 2.595

ZnO (0002) d spacing

0.5 0.0 0.5 1.0 1.5 2.0

O_2/Ar (%)

H_2/Ar Ratio (%)

Separating H_2 and Thickness Effects

ZnO:Al (0.2 wt.%)
Room T, 0.3% H_2/Ar
ZnO (0002) bulk
Fit to d spacing

Int = K0 + (K1)*Thick^(K2)
K0 = 2.595 ± 0.00731
K1 = 0.62272 ± 0.77
K2 = -0.51919 ± 0.247

d spacing (Å)
2.620
2.610
2.600

0 2000 4000 6000
Thickness (Å)

Undoped ZnO
ZnO:Al (0.1 wt.%)
ZnO:Al (0.2 wt.%)
ZnO:Al (0.5 wt.%)
ZnO:Al (1 wt.%)
ZnO:Al (2 wt.%)

y = y0 + A*exp(-(x-x0)/tau))

Thickness (Å)
7000
6000
5000
4000
3000

0.0 0.5 1.0 1.5 2.0
H_2/Ar Ratio (%)

- 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

ZnO film lattice spacing, substrate temp. 200ºC
ZnO undoped
ZnO:Al (0.1 wt.%)
ZnO:Al (0.2 wt.%)
ZnO:Al (0.5 wt.%)
ZnO:Al (1 wt.%)
ZnO:Al (2 wt.%)
ZnO (0002) (JCPDS 36-1451)

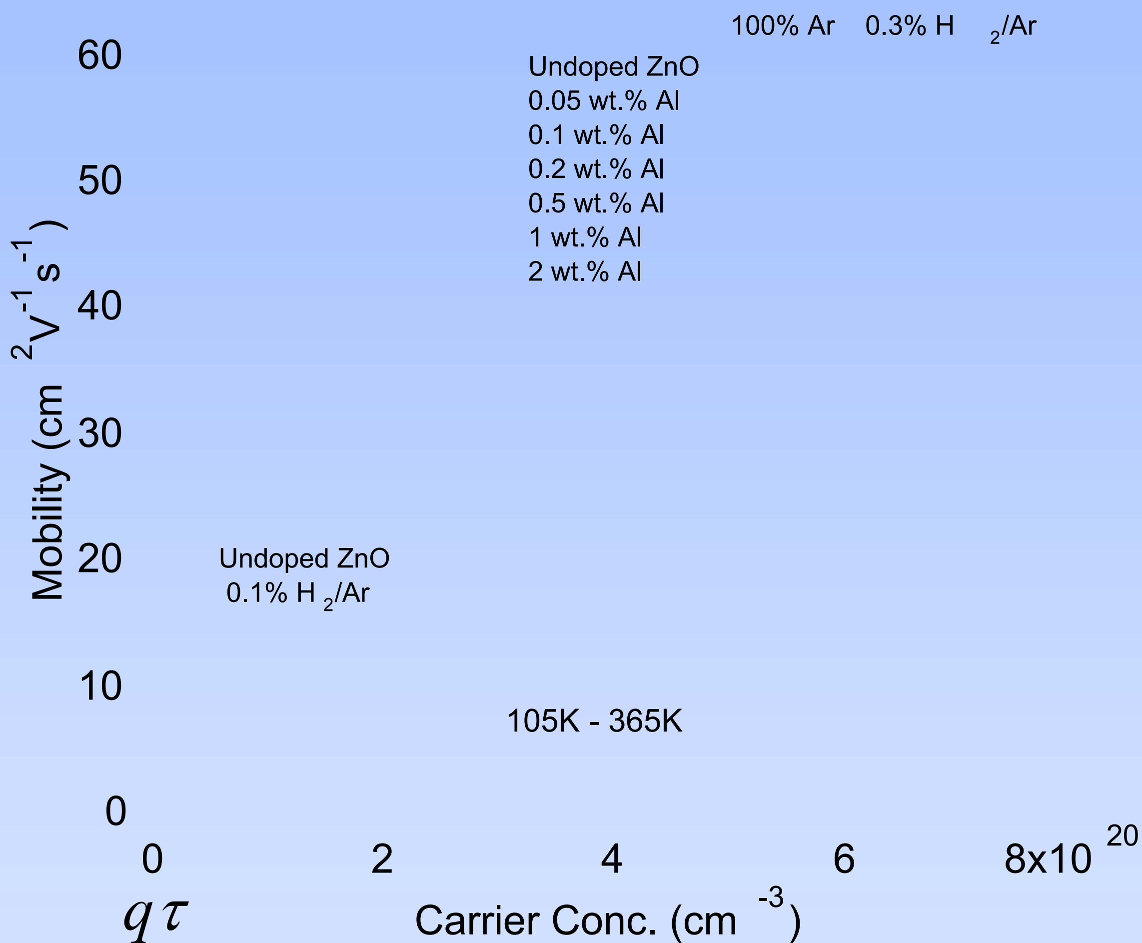
Thickness + H_2

Thickness only

d spacing (Å)
2.630
2.625
2.620
2.615
2.610
2.605
2.600
2.595

0.5 0.0 0.5 1.0 1.5 2.0
O_2/Ar (%) H_2/Ar Ratio (%)

Scattering Mechanisms Using T-dep. Hall



$$\mu = \frac{q\tau}{m^*}$$

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

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

Dopant Ionization - EPMA

Substrate temp. 200ºC
ZnO:Al (0.05 wt.%)
ZnO:Al (0.1 wt.%)
ZnO:Al (0.2 wt.%)
ZnO:Al (0.5 wt.%)
ZnO:Al (1.0 wt.%)
ZnO:Al (2.0 wt.%)
Meas./Spec. Dop./Zn Ratio
5
4
3
2
1
0
0.5 0.4 0.3 0.2 0.1 0.0 0.2 0.4 0.6 0.8 1.0
O_2/Ar Ratio (%)
H_2/Ar Ratio (%)

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

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

Substrate temp. 200ºC
ZnO:Al (0.05 wt.%)
ZnO:Al (0.1 wt.%)
ZnO:Al (0.5 wt.%)
ZnO:Al (1.0 wt.%)
ZnO:Al (2.0 wt.%)
Corrected Ionization (%)
80
60
40
20
0
0.0 0.2 0.4 0.6 0.8 1.0
H_2/Ar Ratio (%)

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

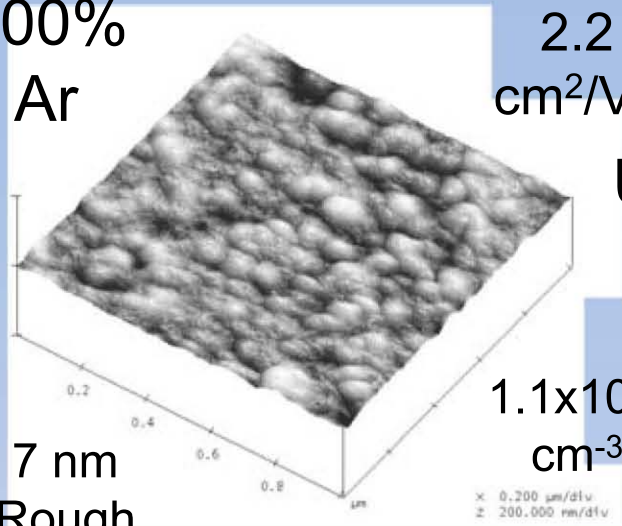
Measurements performed by Bobby To, NREL

Undoped ZnO

1 µm on a side

100% Ar

2.2 cm^2/Vs

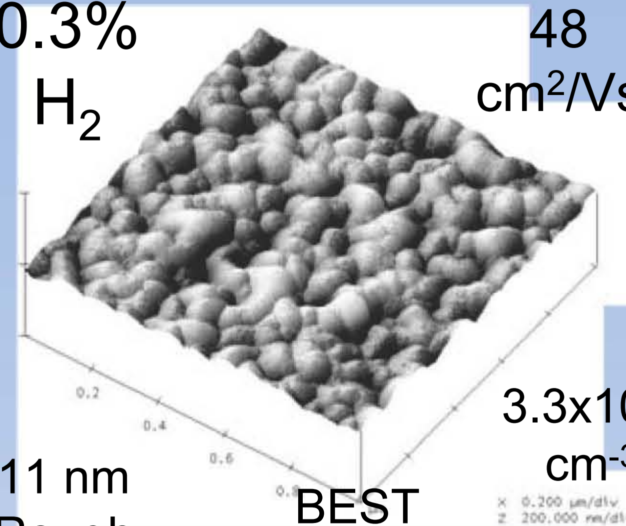


1.1×10^{19} cm^{-3}

7 nm Rough

0.3% H_2

48 cm^2/Vs



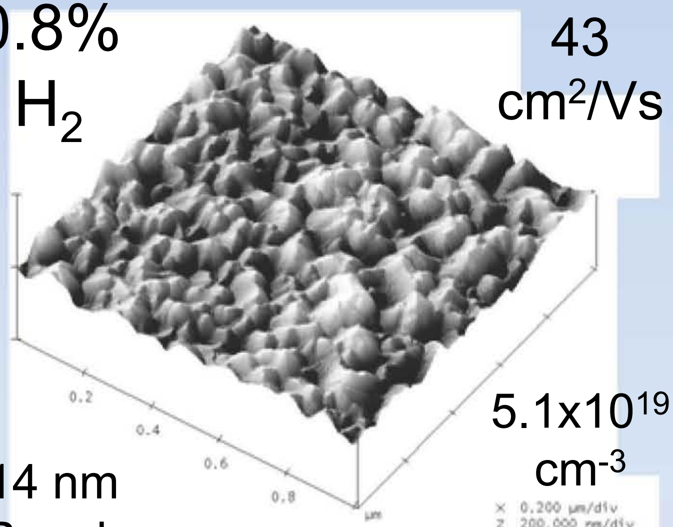
3.3×10^{19} cm^{-3}

11 nm Rough

BEST MOBILITY

0.8% H_2

43 cm^2/Vs

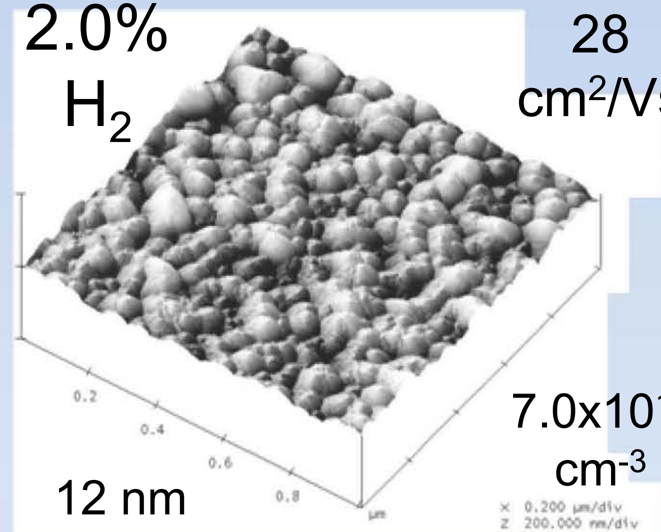


5.1×10^{19} cm^{-3}

14 nm Rough

2.0% H_2

28 cm^2/Vs



7.0×10^{19} cm^{-3}

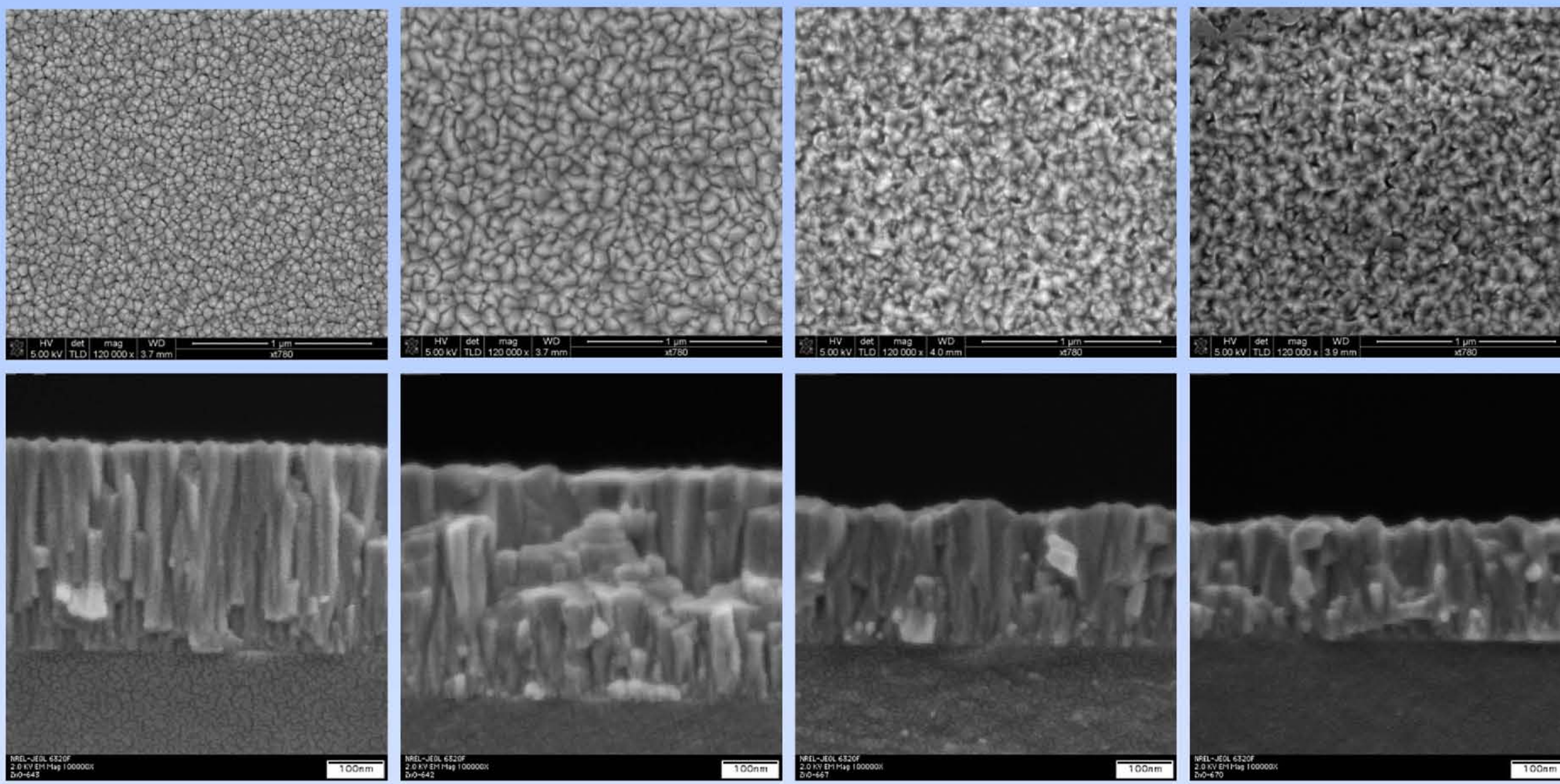
12 nm Rough

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



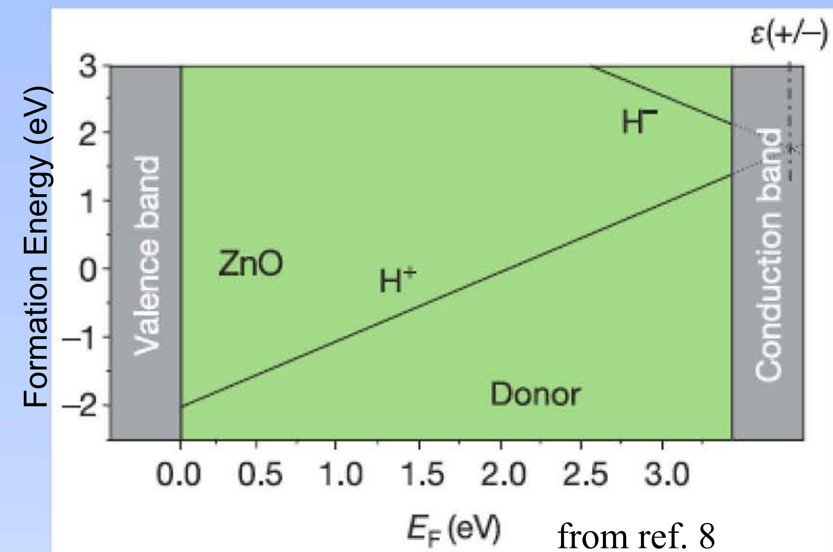
Performed by Bobby To, NREL

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

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[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

Transparent Top Contact

p-layer

p

p

Eg > 1.72 eV
i-layer

1.60 Š Eg Š 1.65

p

Thin film
Si PV

1.40 Š Eg Š 1.45

ZnO

n-layer

Back Reflecting Metal

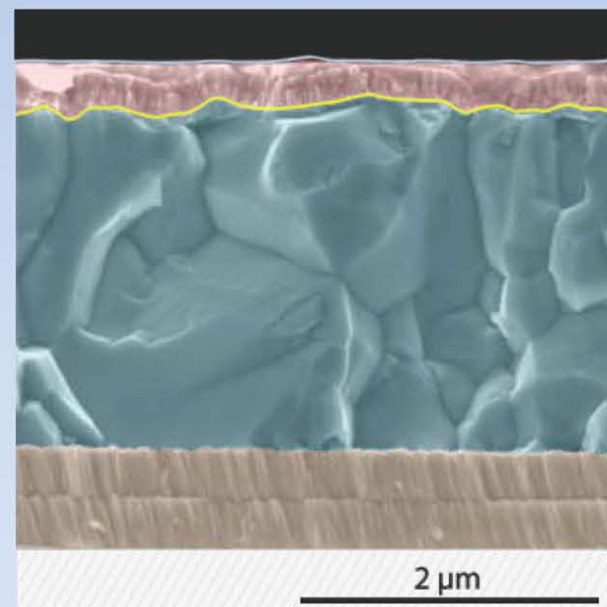
Brent Nelson, NREL

ZnO:Al
1200 Å
CdZnS
~300 Å

CIGS
2.5 µm

Mo
1 µm

Glass,
Metal
Foil,
Plastics



CIGS

R. Noufi, NREL