High-Transparency Sputtered In_2O_3 and ITO Films Containing Zirconium

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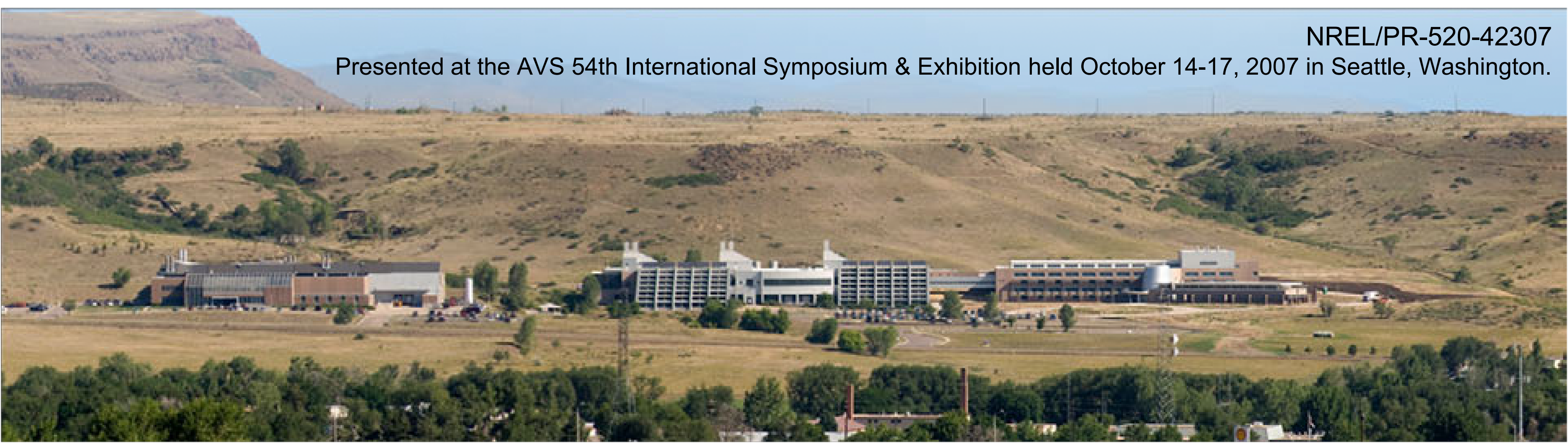

NREL/PR-520-42307
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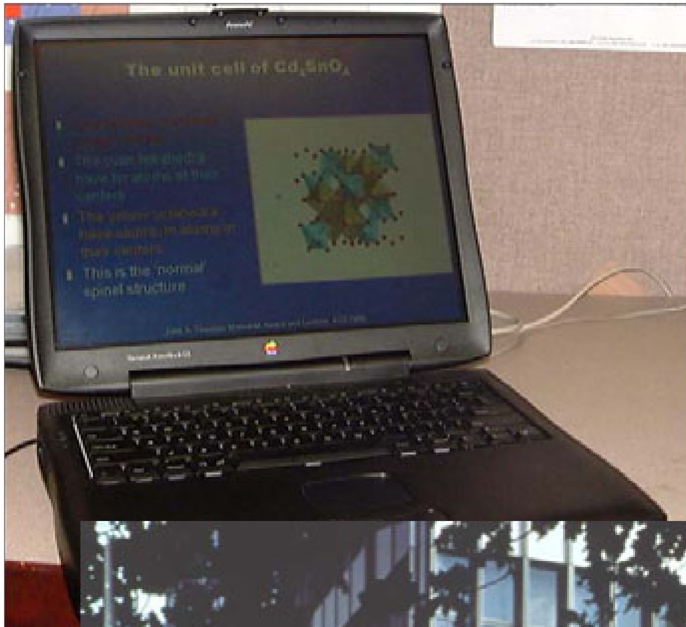
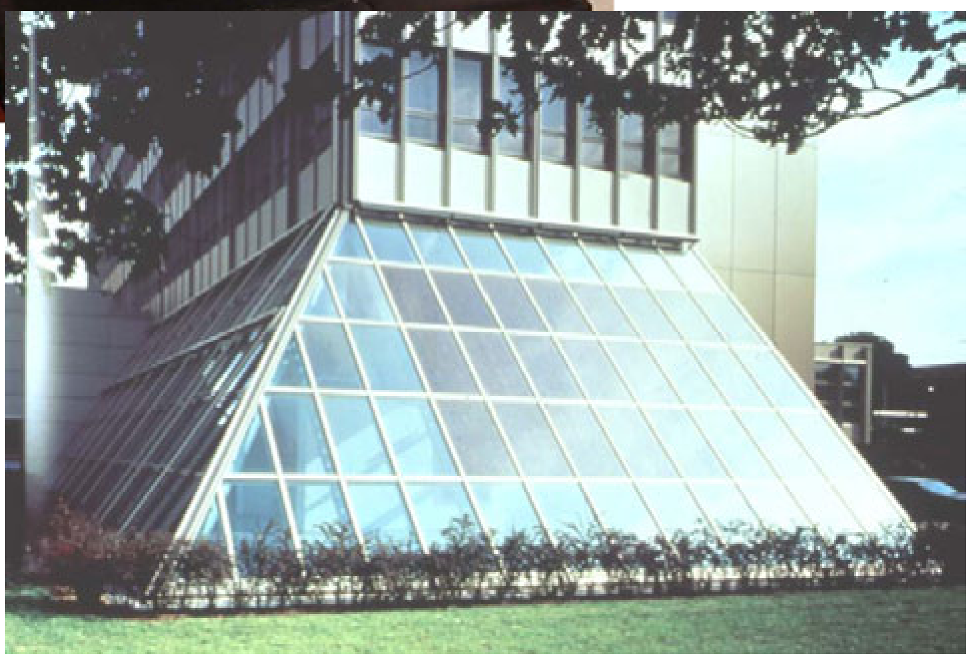
Applications of Transparent Conducting Oxides (TCOs)

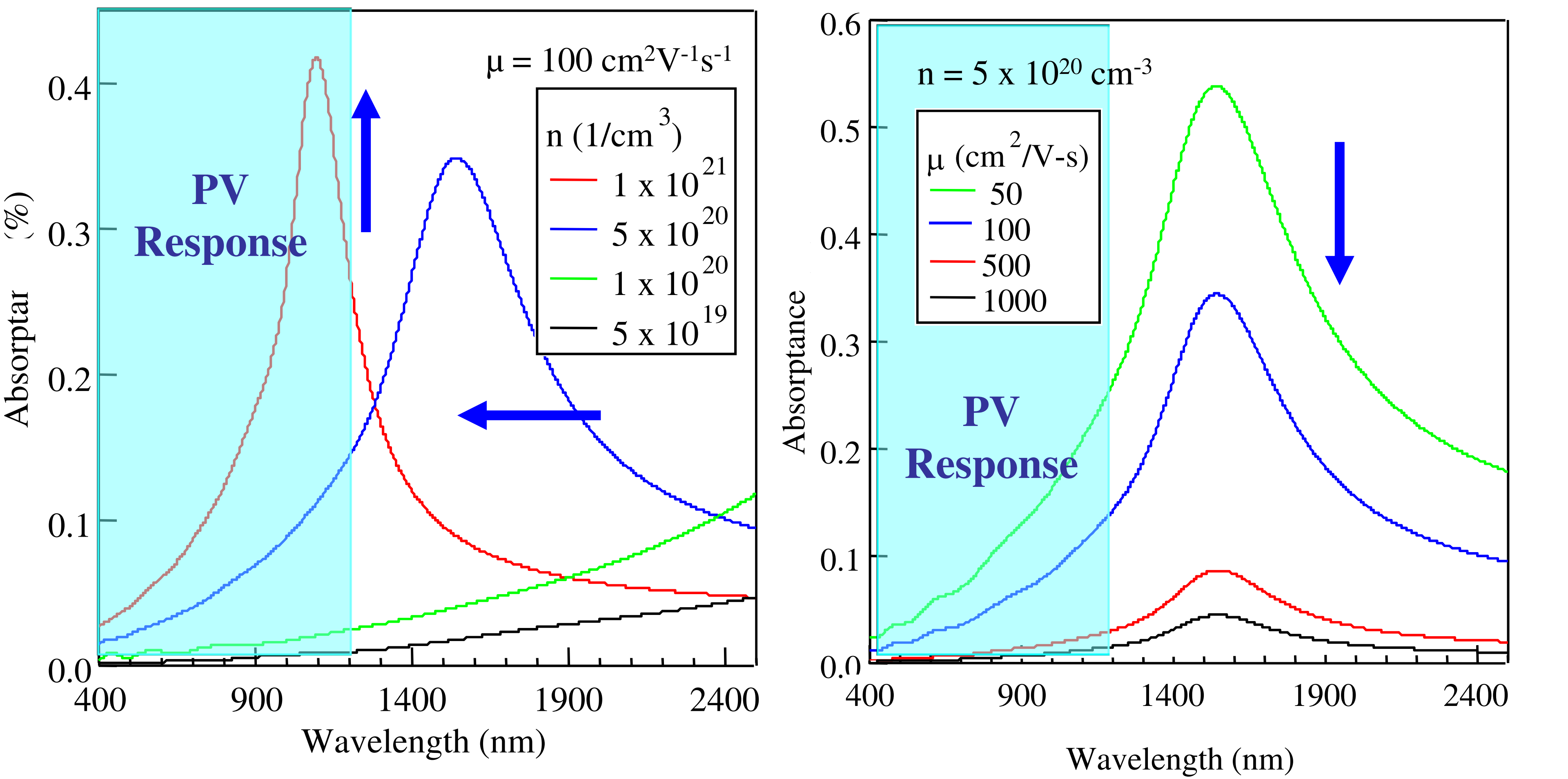




TCOs in Photovoltaic Solar Cells

Effect of Mobility and Carrier Concentration on TCO Absorption

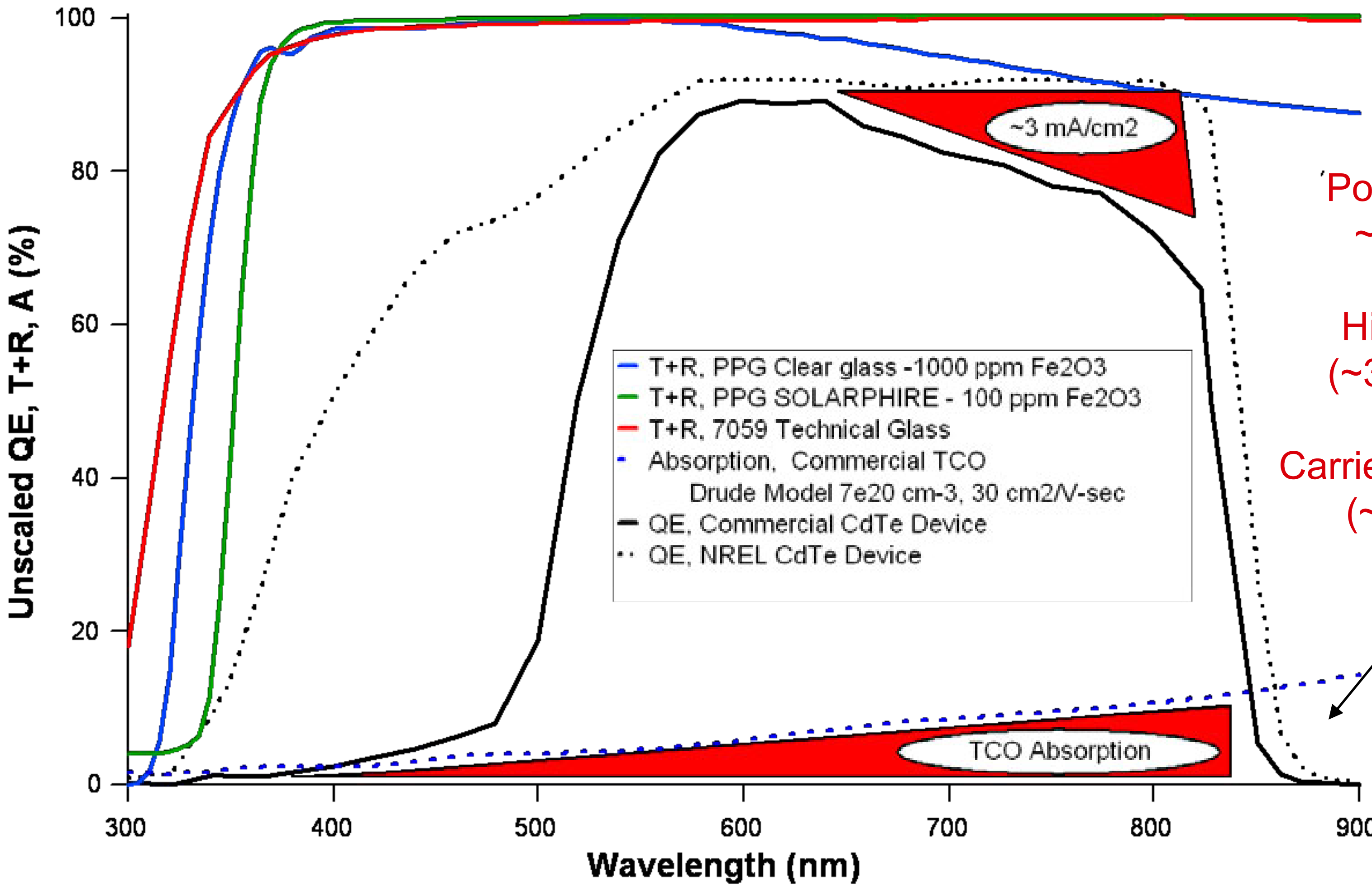
Drude Theory Calculations



T.J. Coutts et. al., MRS Bulletin 25, 58-65 (2000)

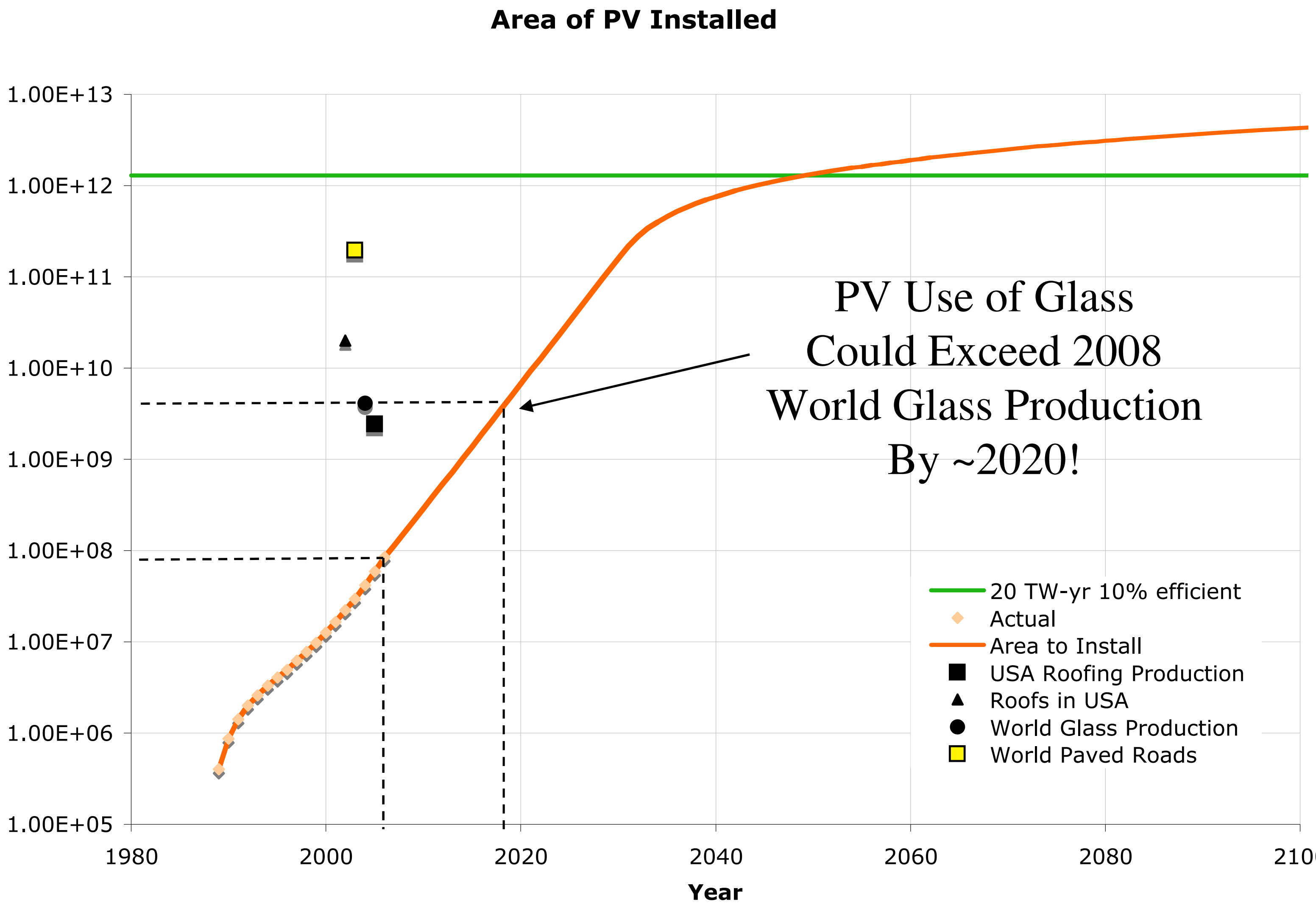
Effect of TCO on PV Module Performance

CdTe PV Module (~850 nm Bandgap)



Potential Gain of ~1.5 mA/cm2 for TCO Higher Mobility (~30 cm2/V-sec) & Lower Carrier Concentration (~2×10^{20} cm^{-3})

How Big a Customer Will PV Be for Commercial Glass?



Source: Brent Nelson, NREL

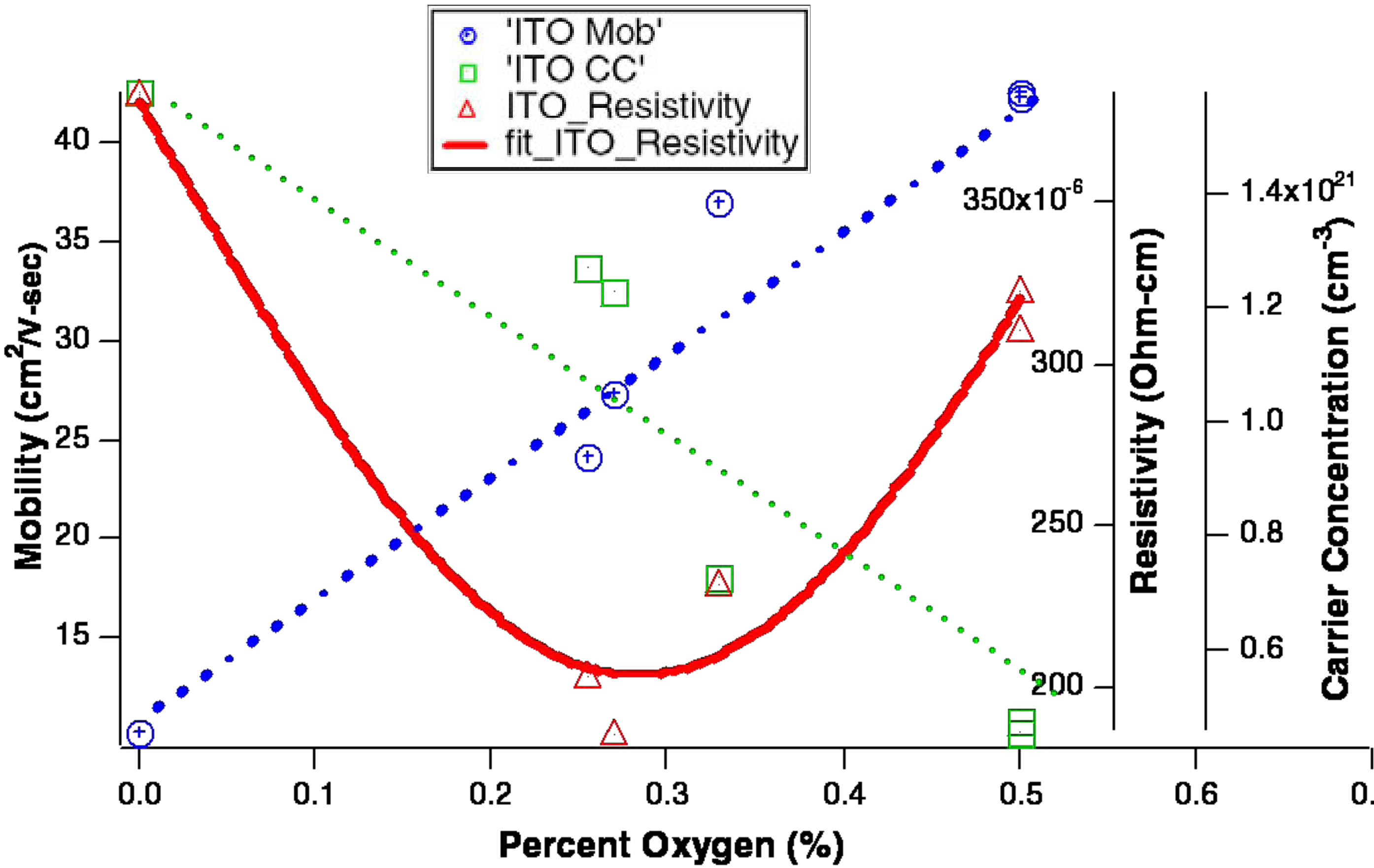
Some Attributes of TCO Coating for PV

- **Inexpensive**
- **Environmentally Stable (30-year lifetime outdoor module)**
- **High-Temperature Stability (>650°C for some applications)**
- **High Mobility (~60-100 cm^2/V-sec)**
  - **Allows for use of lower carrier concentration**
  - **Provides for high NIR transparency**
- **Low Optical Absorption (UV to NIR)**
- ***High Figure of Merit***

$$Figure\ of\ Merit = \frac{\sigma}{\alpha} = \frac{Electrical\ Conductivity}{Optical\ Absorption}$$

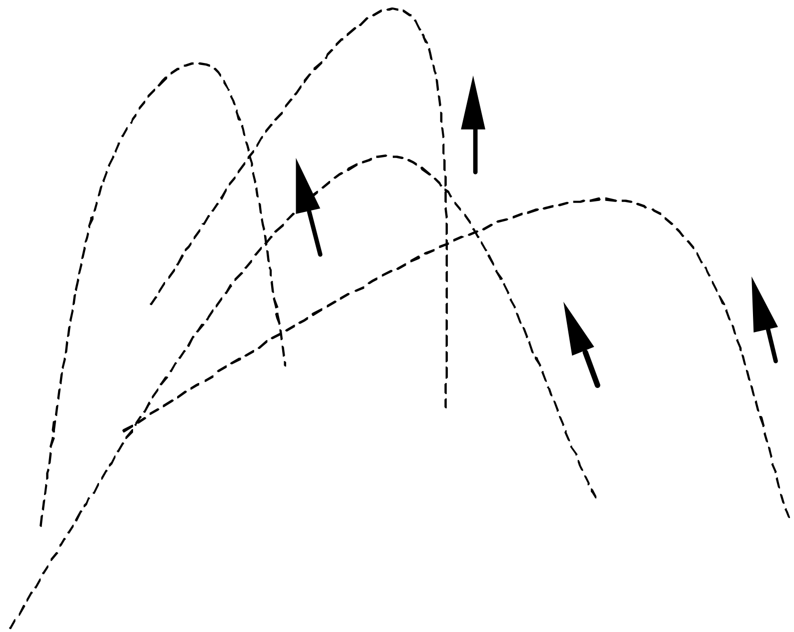
$$\sigma = ne\mu = \frac{ne^2\tau}{m^*}$$

For ITO produced by sputtering, optimum electrical properties are achieved through careful control of oxygen partial pressure during deposition



Background

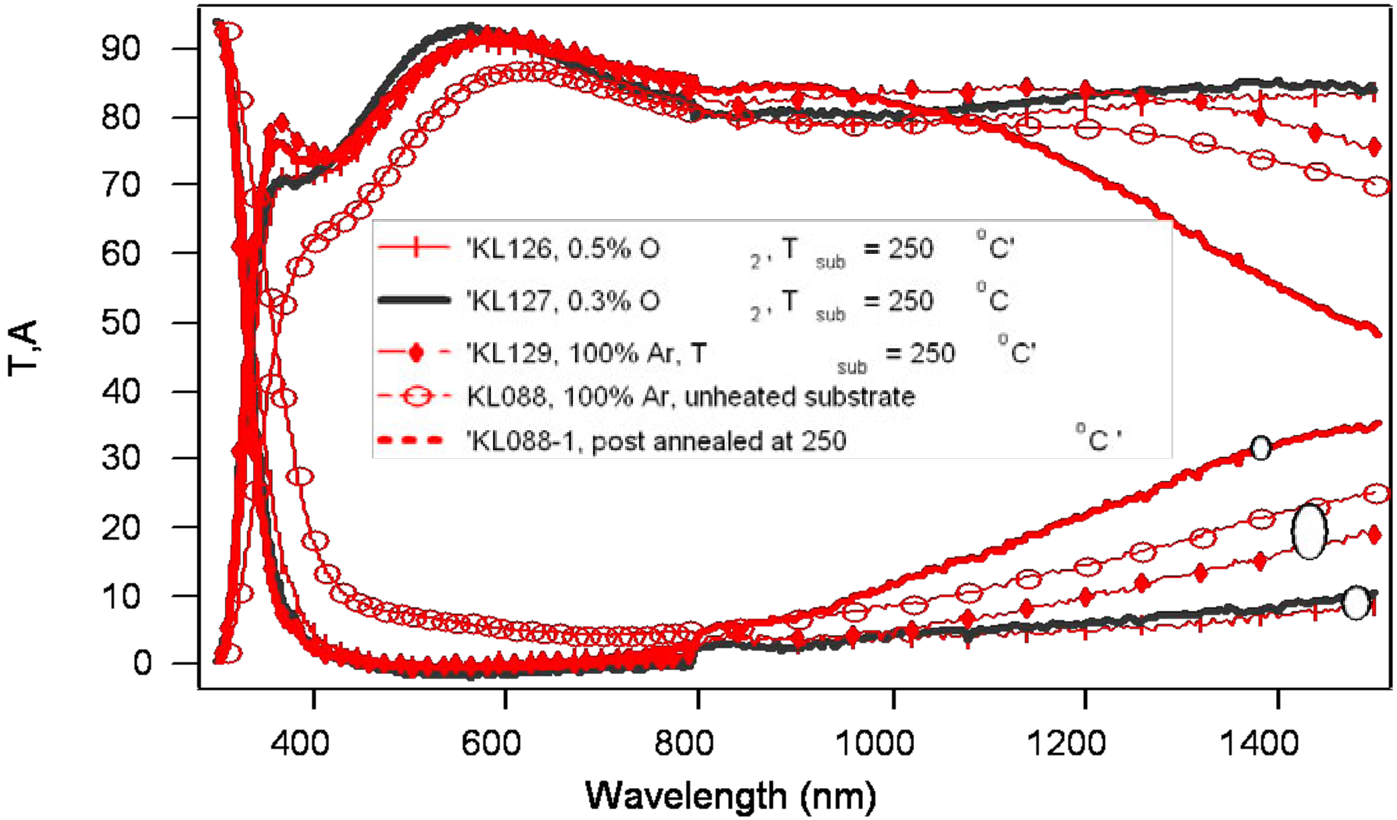
$In_2O_3:Mo$



From Yoshida et. al, APL 84 (12) (2004).

Requirement for High Optical Quality in ITO

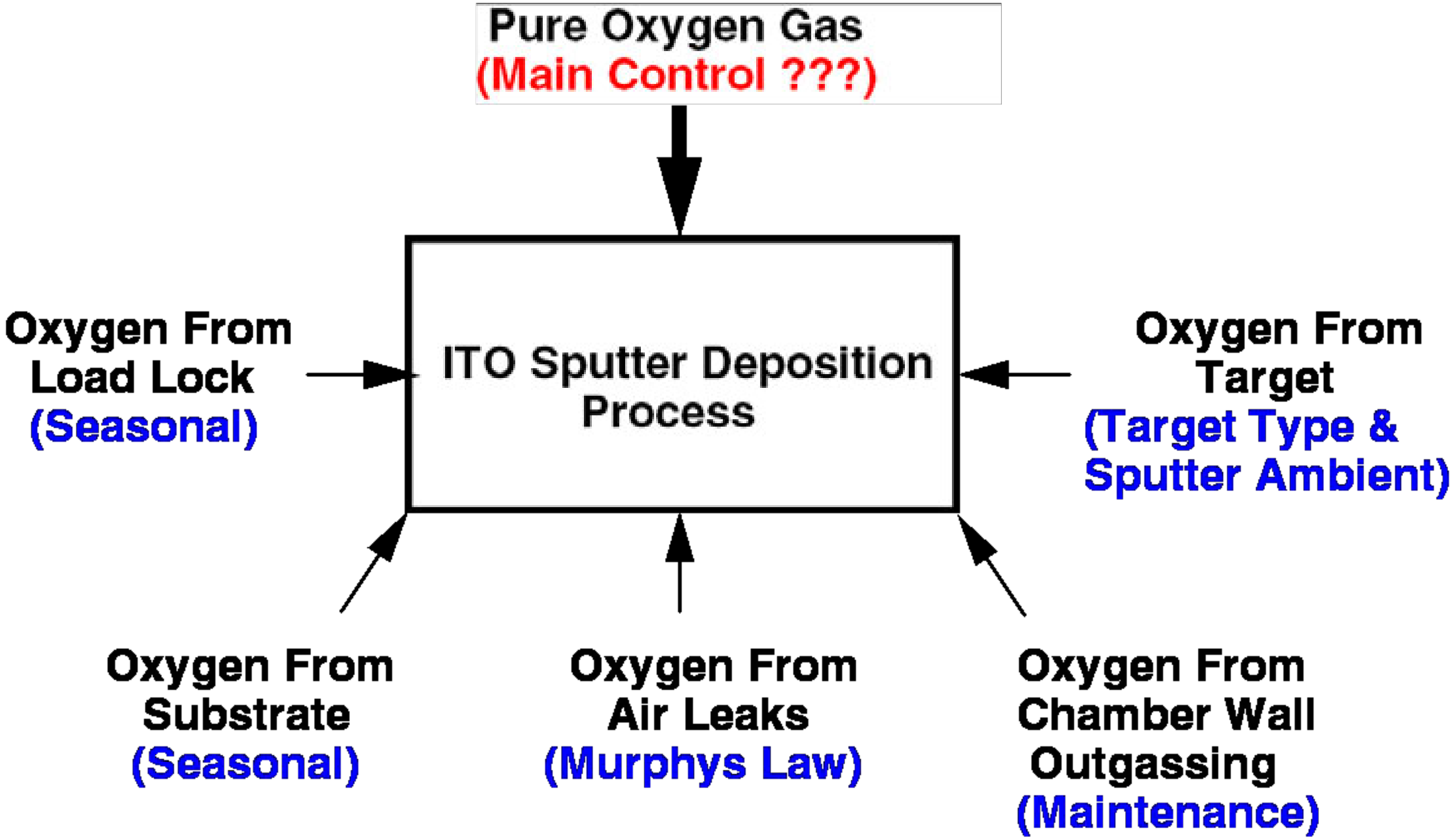
Add just enough oxygen to produce good optical quality, while not sacrificing electrical conductivity



Increasing Oxygen During Deposition

From Zhou,Wu, Gessert, et al. 05 Spring MRS

Sources of Oxygen in Typical TCO Sputtering Process



Question

Can we make the electrical and optical quality of TCO's
less sensitive to oxygen?

$$Figure\,of\;Merit = \frac{\sigma}{\alpha} = \frac{ne^2\tau}{m^*} = \sqrt{\varepsilon_1} c \varepsilon_o \tau^2 \omega^2$$

$$\varepsilon_1 = \varepsilon_\infty - \frac{ne^2}{\varepsilon_o m^* \omega^2}$$

Add a High-Permittivity Component to TCO

Many previous studies for dielectric materials for MOS devices (e.g., SiO_2 + Zr)

Fewer studies on TCOs (some shown)

- R. Groth, Phys. Stat. Sol. 14 (1966)
- S.B. Qadri et. al., TSF 377 (2000)
- H. Kim et. al, APL 83 (2003)
- T-F. Chen et. al, APL 85 (2004)
- T. Koida et. al., APL 89 (2006)

Part of larger study comparing various dopants in In_2O_3 films

- Group 6A (Mo),
- Group 4A (Ti, Zr, Hf)
- Group 4B (Sn, Pb)

Permittivity Change for Zr in SiO_2

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

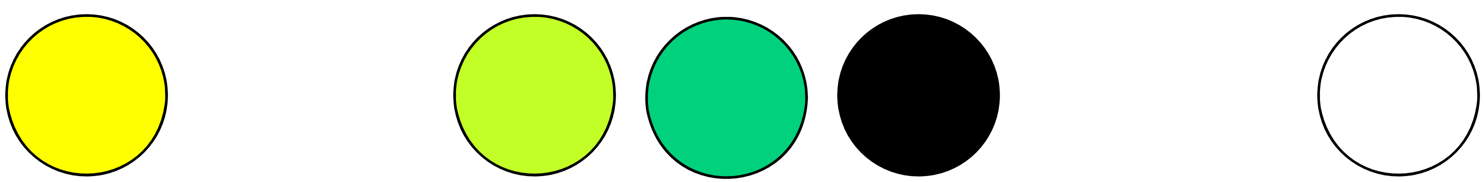
From Lucovsky and Rayner, APL 77 (18) 2912 (2000)

ITO + Zr Related Experiment

- Use r.f. sputtering of pressed-powder targets
  - Corning 1737 Glass
  - Ar or Ar/O_2 ambients
  - 350°C substrate temperature

- Custom-fabricated ITO-like, targets where SnO_2 component replaced by ZrO_2 (91 wt.% In_2O_3 + 9 wt.% ZrO_2)

- Noticed In_2O_3 sputtering targets containing ZrO_2 (IZrO) were significantly different (visually) from other In_2O_3 and ITO targets.



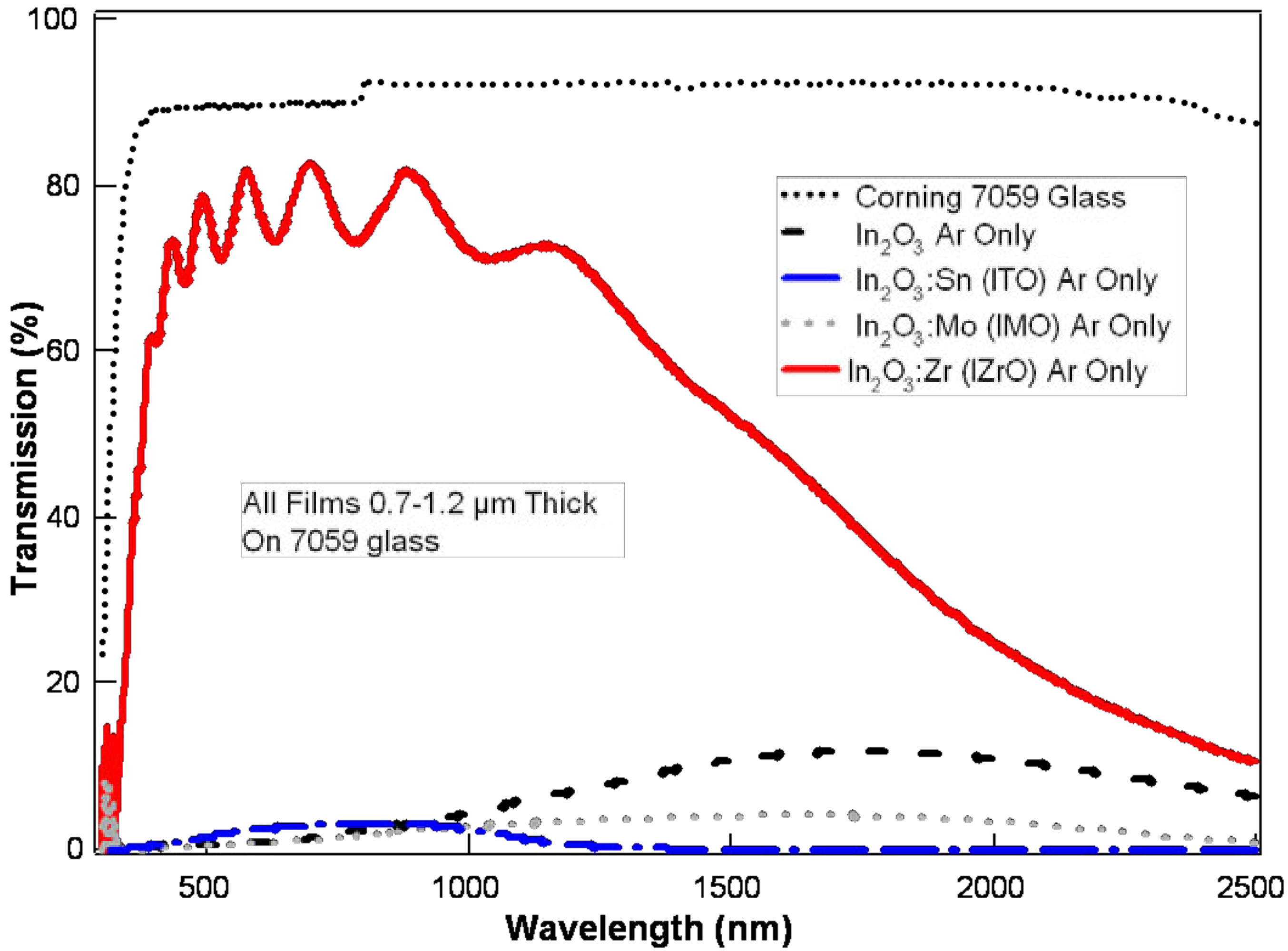
In_2O_3 Targets (1400°C O_2)

ITO Targets (1400°C O_2 and Reduced)

IZrO Target (1400°C O_2)

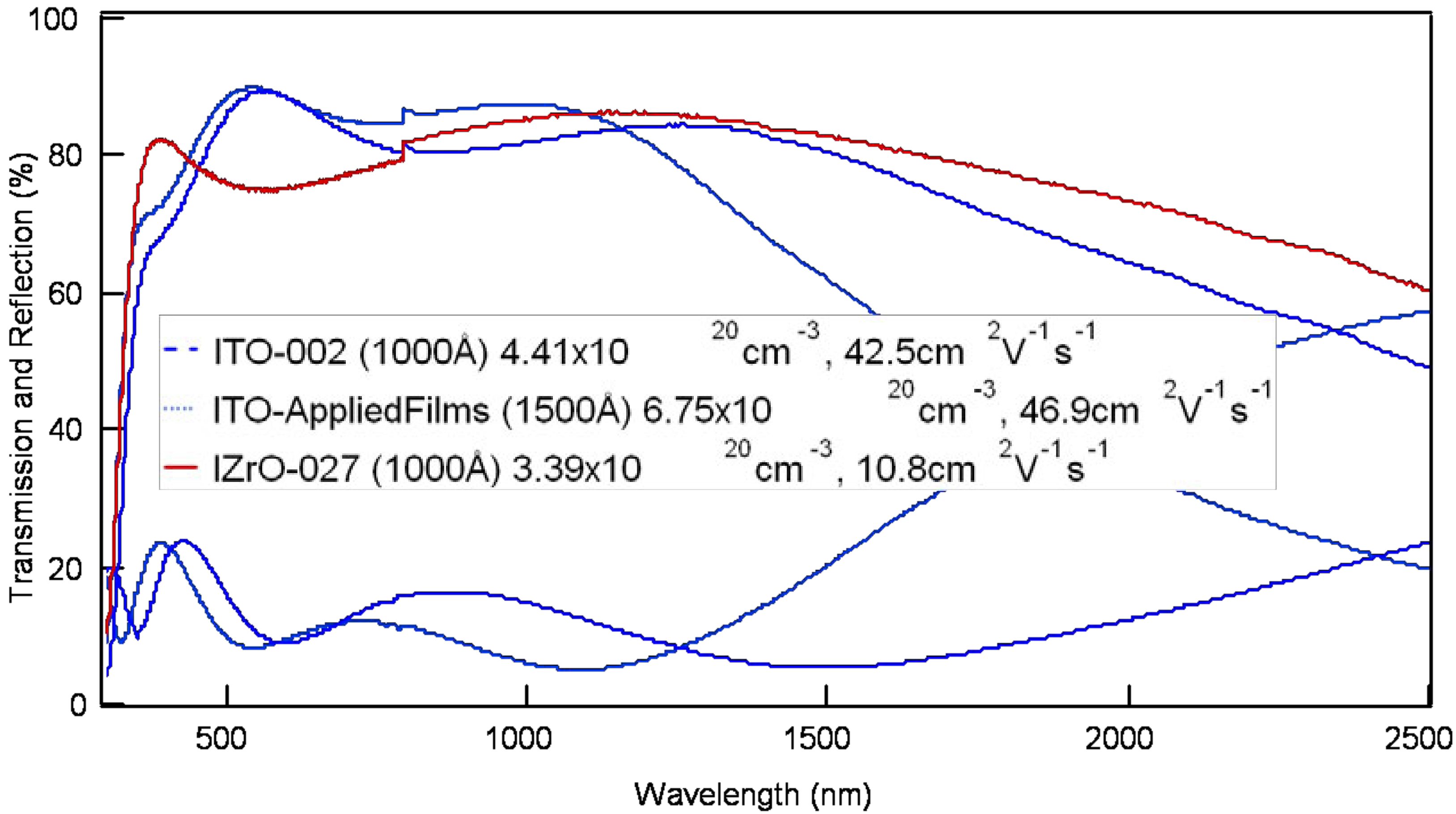
Comparison of TCO Films in Pure Ar

(Note IZrO Target already used for 19 depositions!)



Results

Comparison of IZrO (Pure Ar) with Optimum ITO (Ar/O_2)



Logical Extension of Initial Work

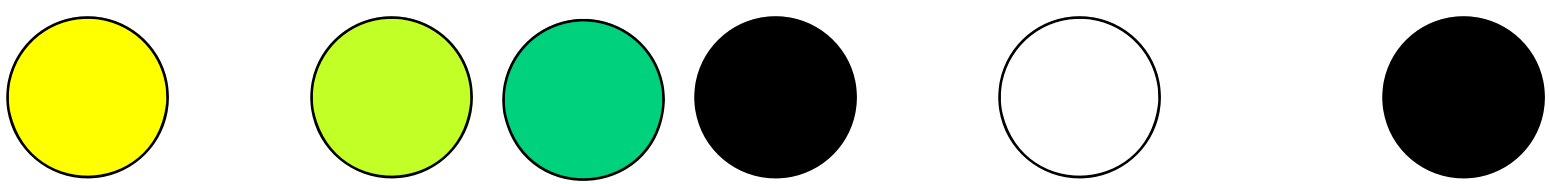
The Next Idea

Is it possible to make the optical properties of traditionally doped TCO material less sensitive to oxygen partial pressure by adding a small amount of ZrO_2 to the target?

Test Procedure

Order a custom In_2O_3:Sn sputtering target that contained 1 wt.% ZrO_2 (90 wt.% In_2O_3 + 8 wt.% SnO_2 + 1 wt.% ZrO_2) We call this material In_2O_3:Sn:Zr or ITZO.

Produce ITZO films and compare to ITO films of similar electrical properties.



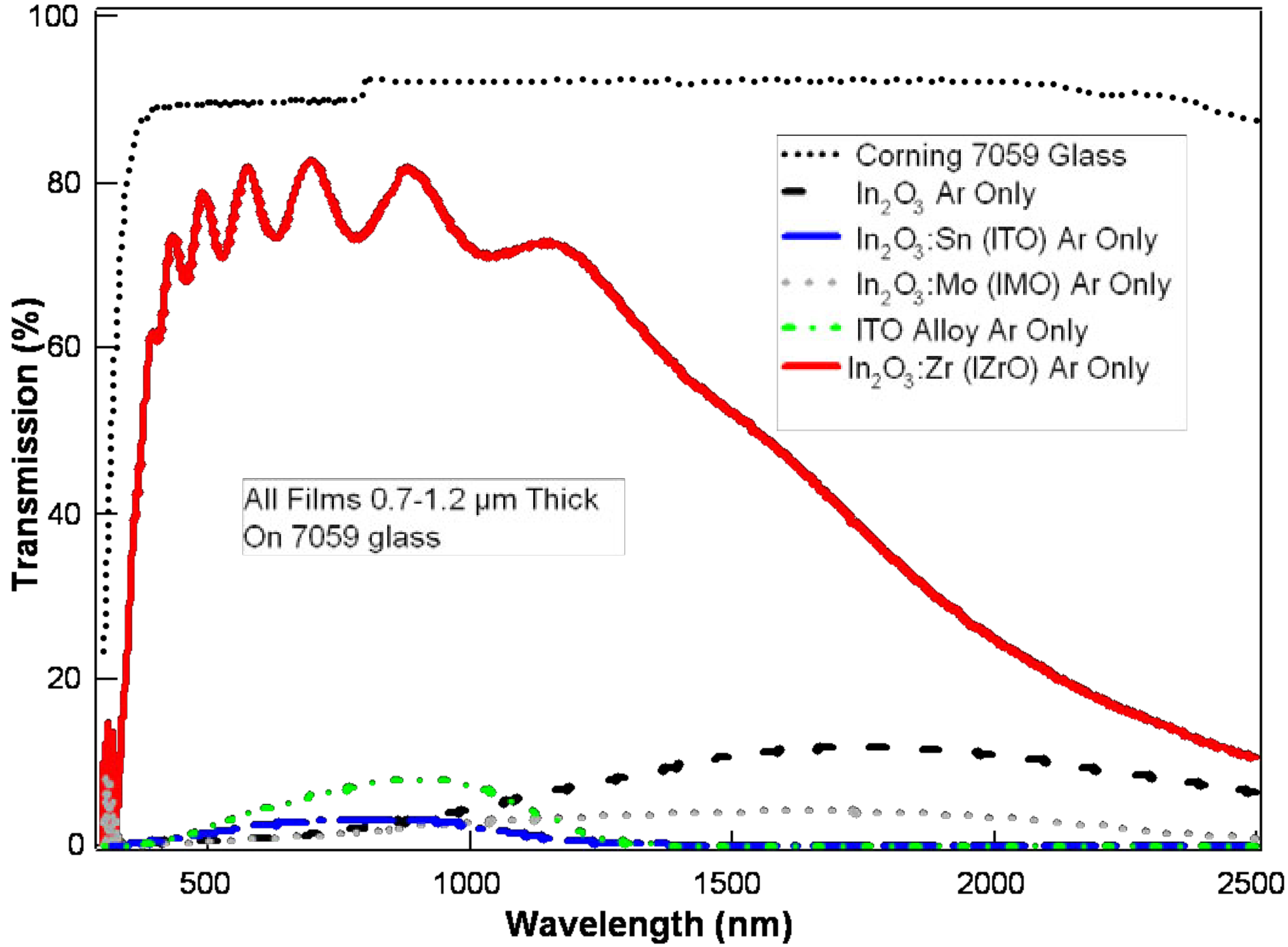
In_2O_3 Targets (1400°C O_2)

ITO Targets (1400°C O_2 and Reduced)

IZrO Target (1400°C O_2)

ITZO Target (1400°C O_2)

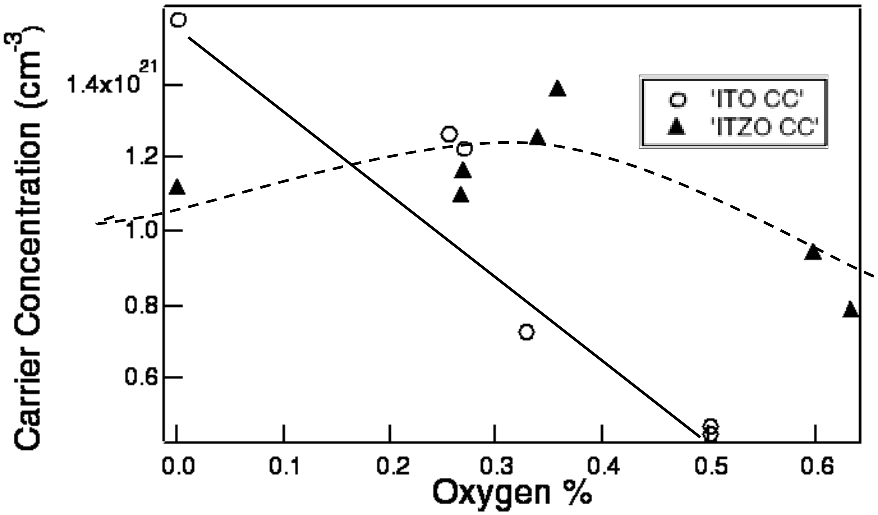
More Comparisons of TCO Films Grown in Pure Ar
ITZO Film in Pure Ar Better Than ITO

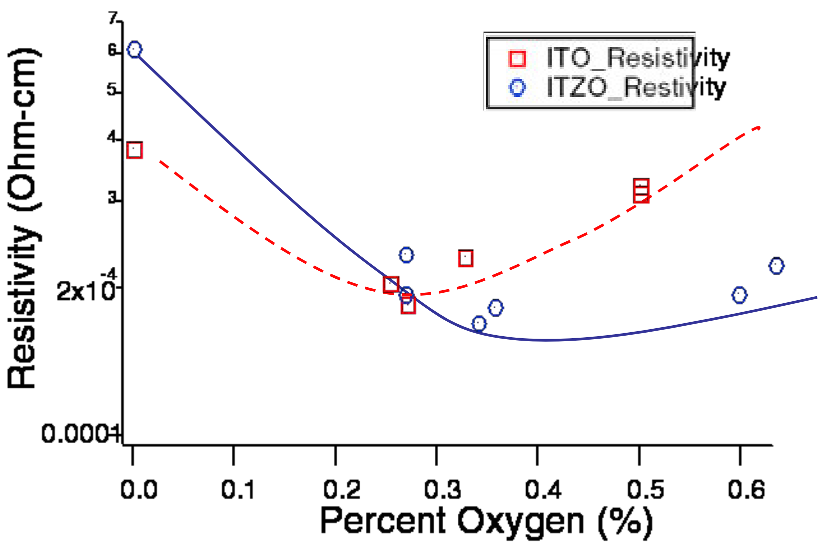


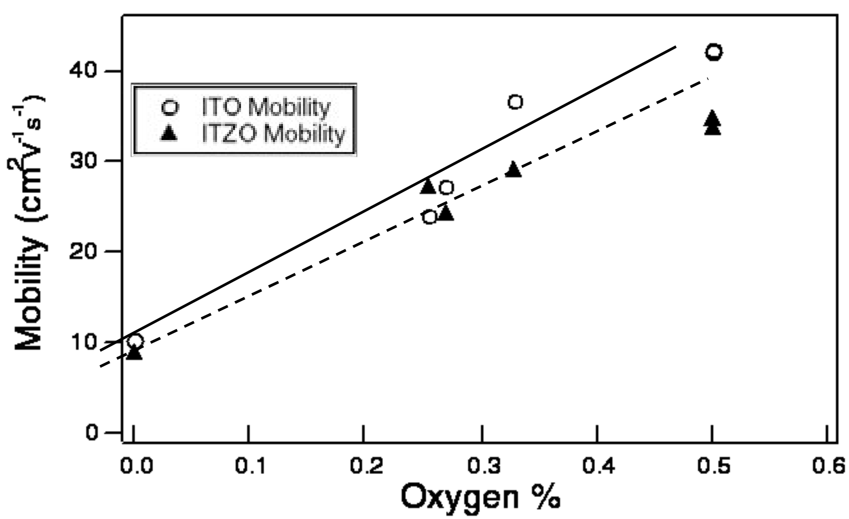
ITZO Results

Comparison of Optimized ITO and ITZO

Adding 1 wt% ZrO_2 to a standard ITO target makes the electrical properties less sensitive to oxygen partial pressure!

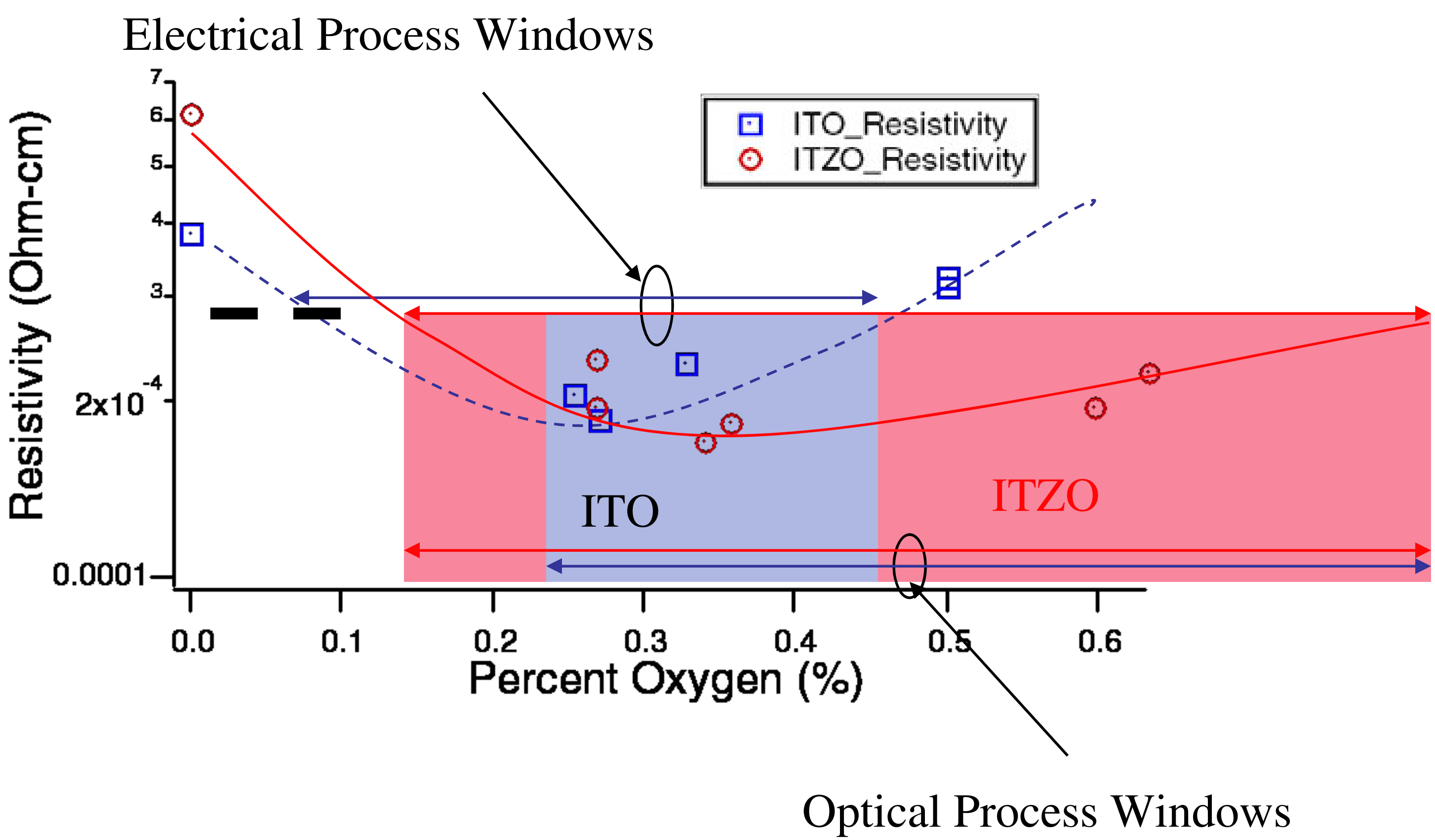






Which TCO Film Would You Want For Your Large-Scale Production Facility?

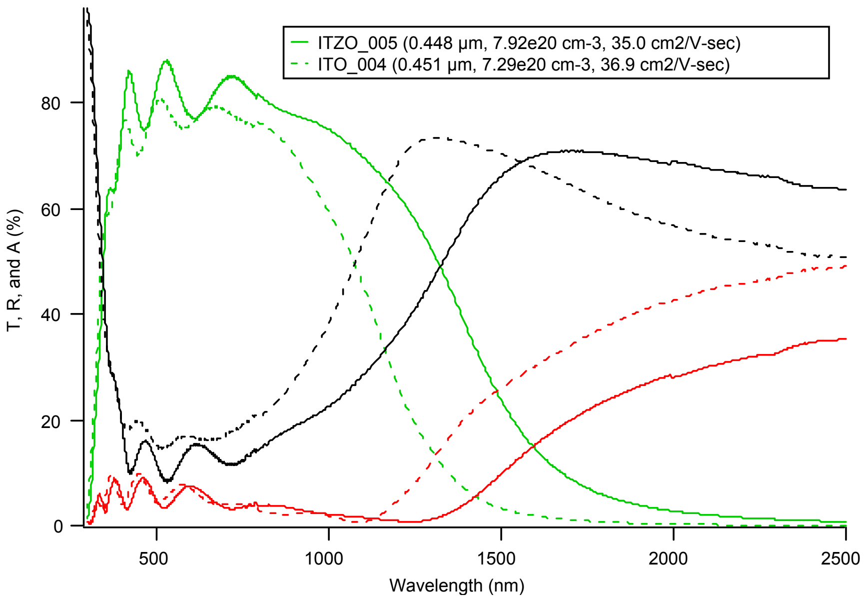
Figure shows that the the combination of electrical and optical properties of ITZO (Red Widow) can be optimized over a much wider range of oxygen partial pressure than ITO (Blue Window) for a given resistivity value (~3x10^{-4} Ohm-cm shown)



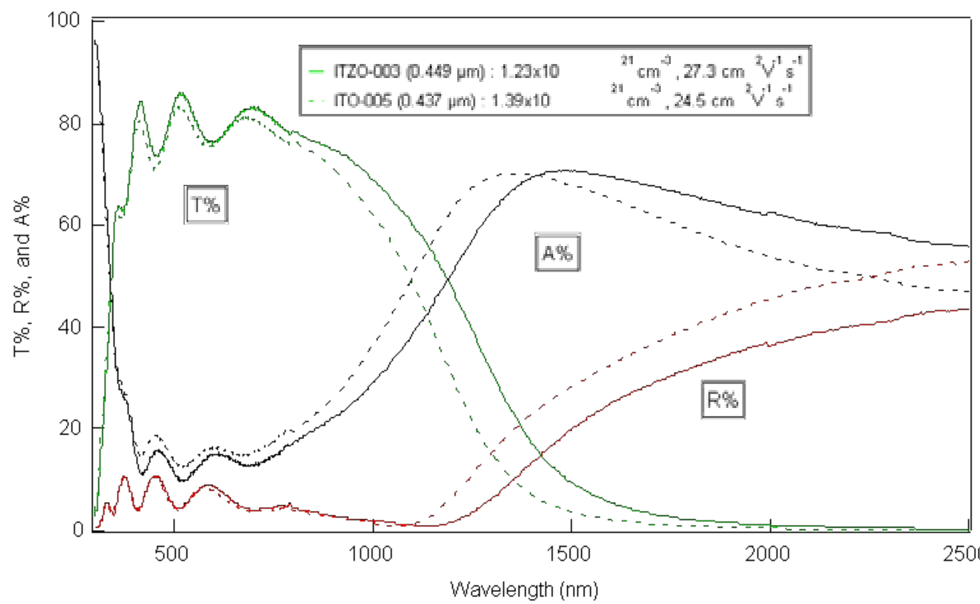
Comparison of TCO Films Deposited at Similar Oxygen Partial Pressure

Results show significantly different IR transmission can result for films with very similar electrical properties

$n = \sim 7 \times 10^{20}\ cm^{-3}$

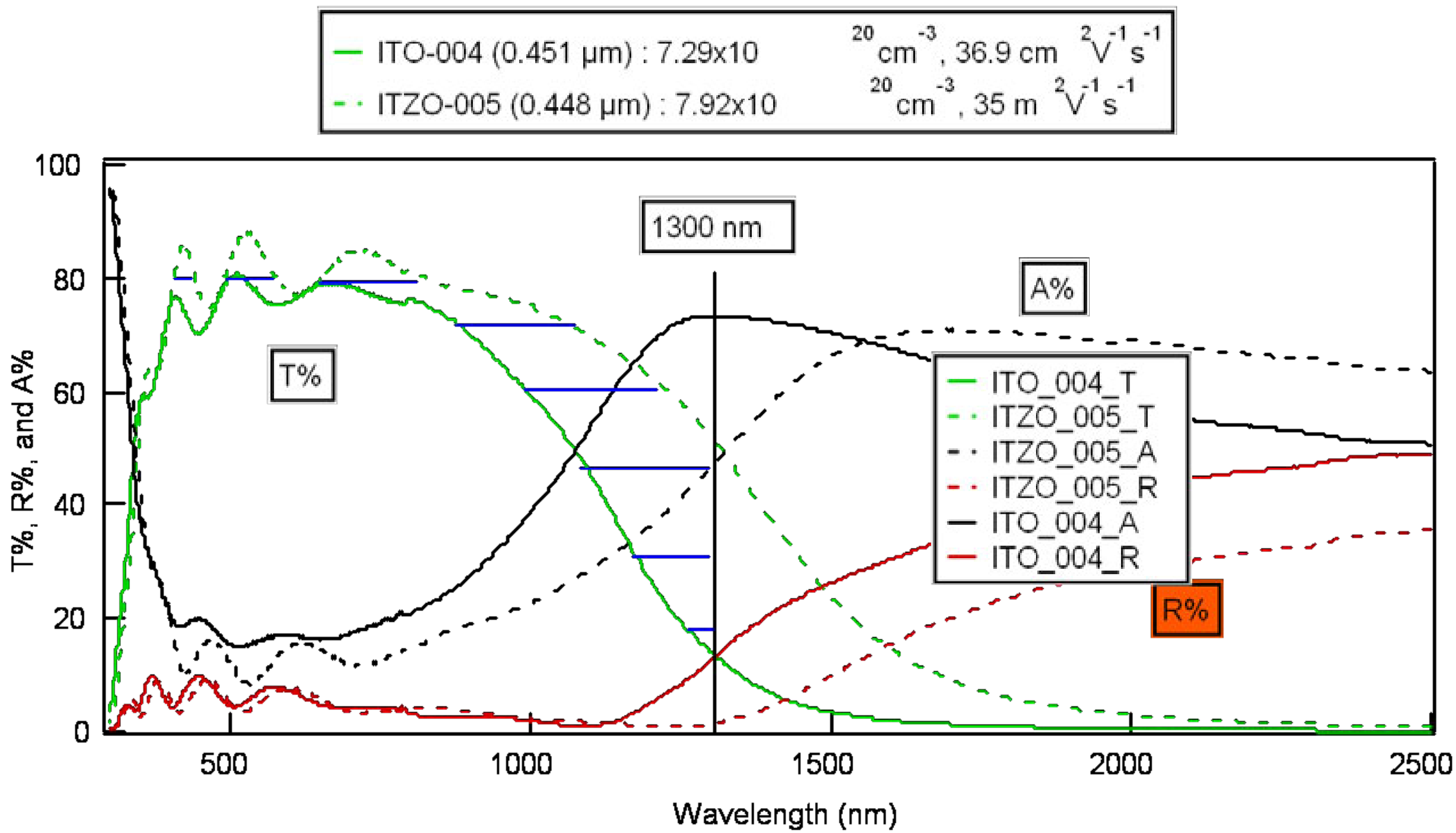


$n = \sim 1.3 \times 10^{21}\ cm^{-3}$



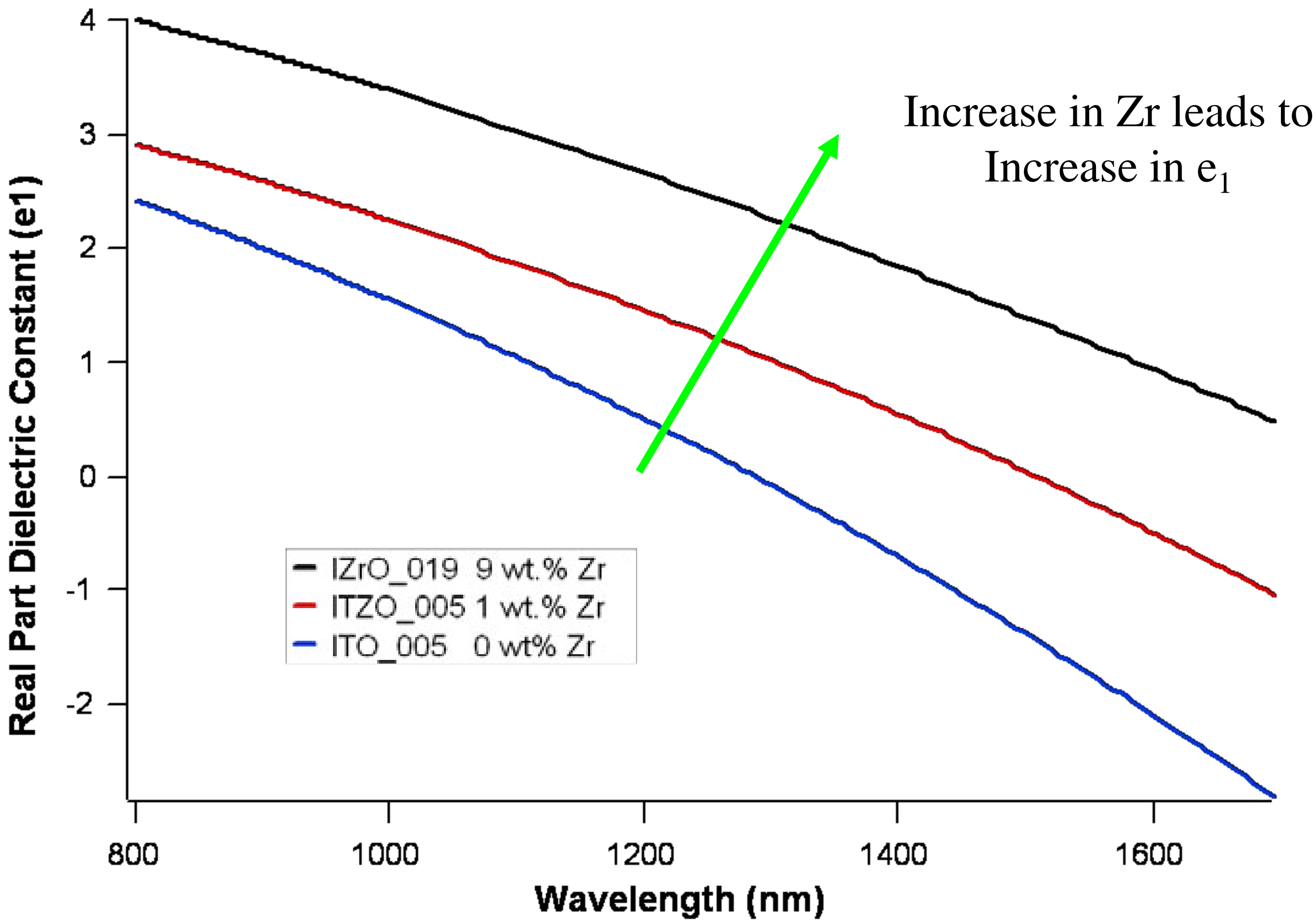
$$\varepsilon_1 = \varepsilon_\infty - \frac{ne^2}{\varepsilon_o m^* \omega^2}$$

Ramifications for the Photovoltaic Application



Does the Permittivity Really Increase?

Wavelength-Scanning Ellipsometry Values of Real Part of Dielectric Constant Near Glass/TCO Interface



1. Adding ZrO_2 to and ITO target produces films that maintain high transparency at low oxygen partial pressures - *AND*

2. Adding ZrO_2 to and ITO target produces films that maintain high carrier concentration at higher oxygen partial pressures. This benefits can be used to widen the process window during TCO production

3. High quality sputtered In_2O_3:Zr films can be produced in pure Ar

4. Adding ZrO_2 to an ITO target improves film transparency beyond that typically expected from Drude theory. This appears to be due to an increase in the dielectric constant, and will may have significant applications for devices like photovotaic solar cells

5. These results are likely true for other refractory metal dopants (e.g., Hf), and for other TCO host materials (e.g., SnO_2, ZnO, $CdSn_2O_4$, etc.)

What's Going On? (Some Speculation)

1. At low levels of ambient oxygen, addition of Zr (or similar materials) to the In_2O_3 matrix (or similar TCOs) may *limit the formation of low-transparency phases* when the sputtering ambient cannot supply sufficient oxygen. Luckily, because Zr is also an effective donor in In_2O_3, *both electrical and optical quality are maintained* at low oxygen partial pressure.

2. At high levels of ambient oxygen, addition of Zr (or similar materials) to the In_2O_3 matrix *may getter excess oxygen* into strong ZrO_2 bonding, allowing oxygen vacancies in the In_2O_3 lattice to be retained as donors. This may be similar to the gettering process in non-evaporative getter (NEG) materials where Zr is also used. This could allow electrical resistivity to remain low at high oxygen partial pressures.

3. Both these results can provide *advantages in a TCO production environment* because the range of oxygen partial pressure where optimum films are produced is extended, and because optimization is enabled by the target composition rather than the (unpredictable) sputtering ambient.