

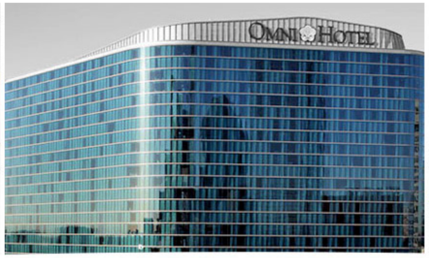

PPG Flat Glass
Bringing innovation to the surface.™

Chemical Vapor Deposition of Coatings On Glass

J.W. McCamy

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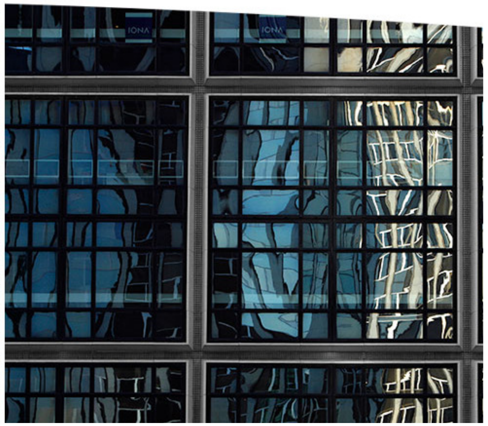

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Outline

- Materials and Coating Design for Architectural Applications
- Process and Equipment
- Deposition Mechanisms
- Materials and Coating Design for Solar Applications

Needs and wants
Characteristics
Constraints

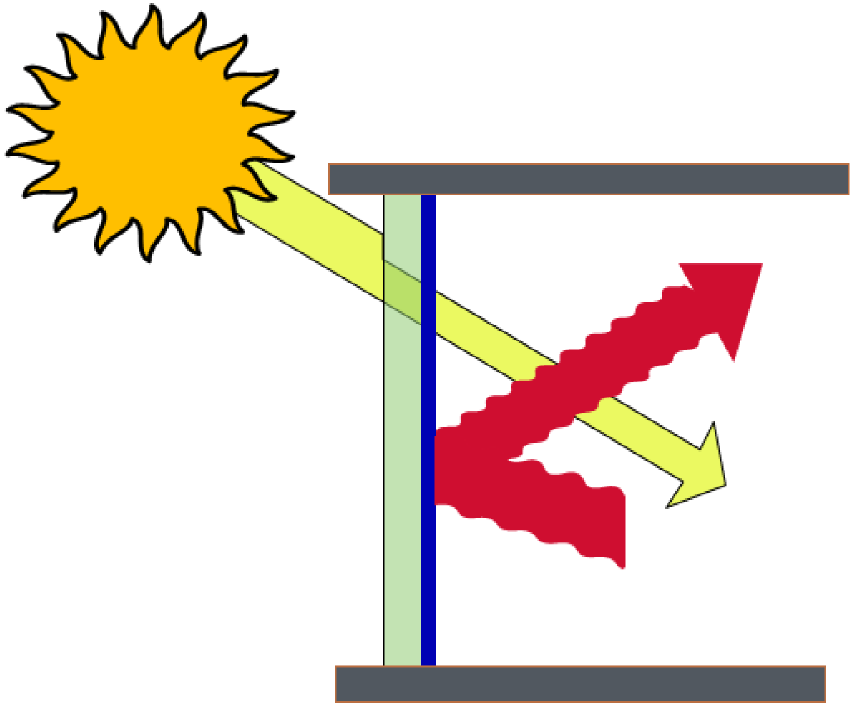
Materials and Design for Architectural Applications

Coatings functions and characteristics

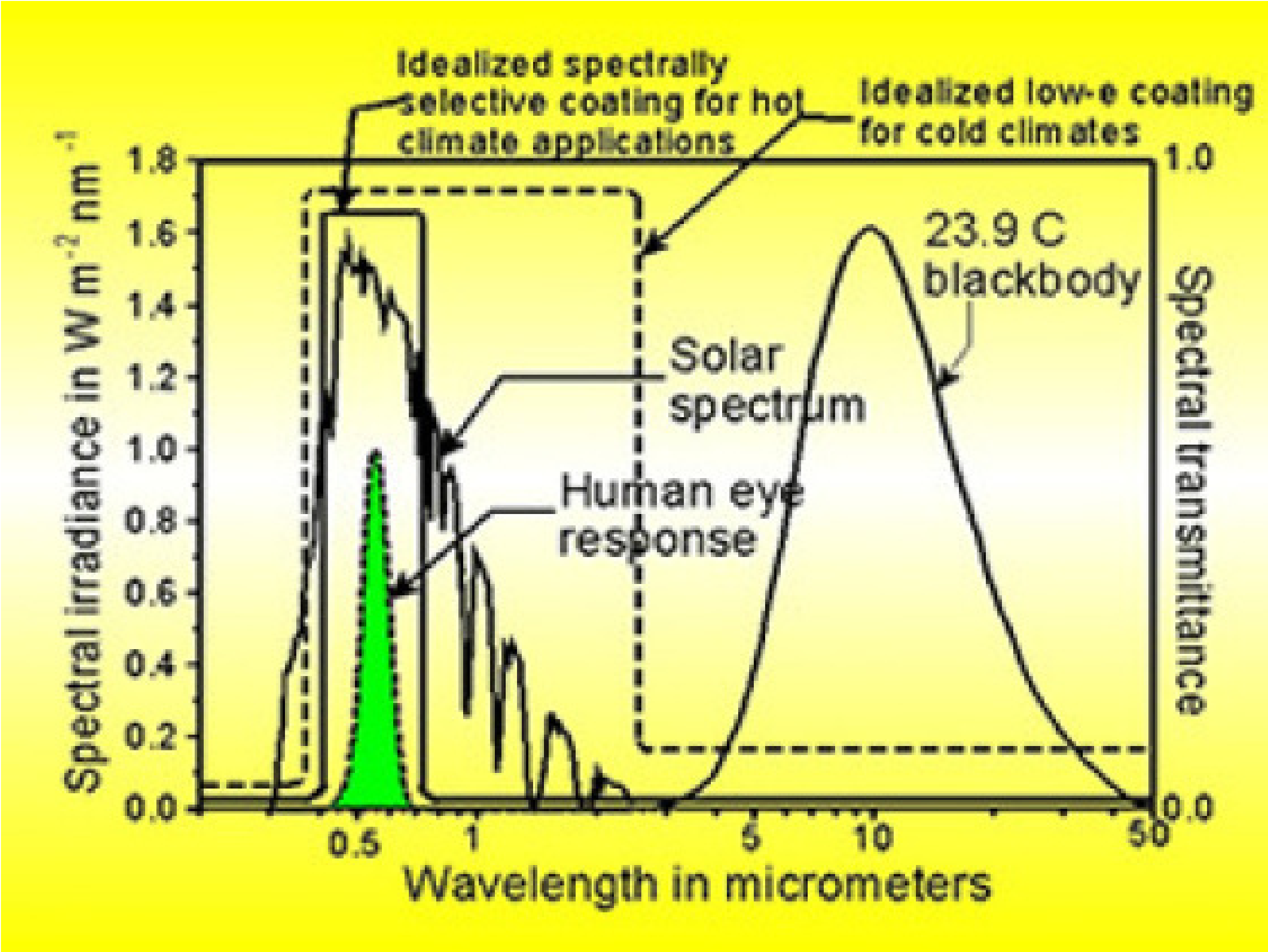
- **Heat management**
- **Color / aesthetics**

Materials and Design

- **Visible transmission**
  - As high as possible
  - VLT ~ 75% (typ.)
- **Heat management for architectural applications**
  - Thermal
  - Solar control
- **Reflection**
  - Codes in many major cities specify <20%

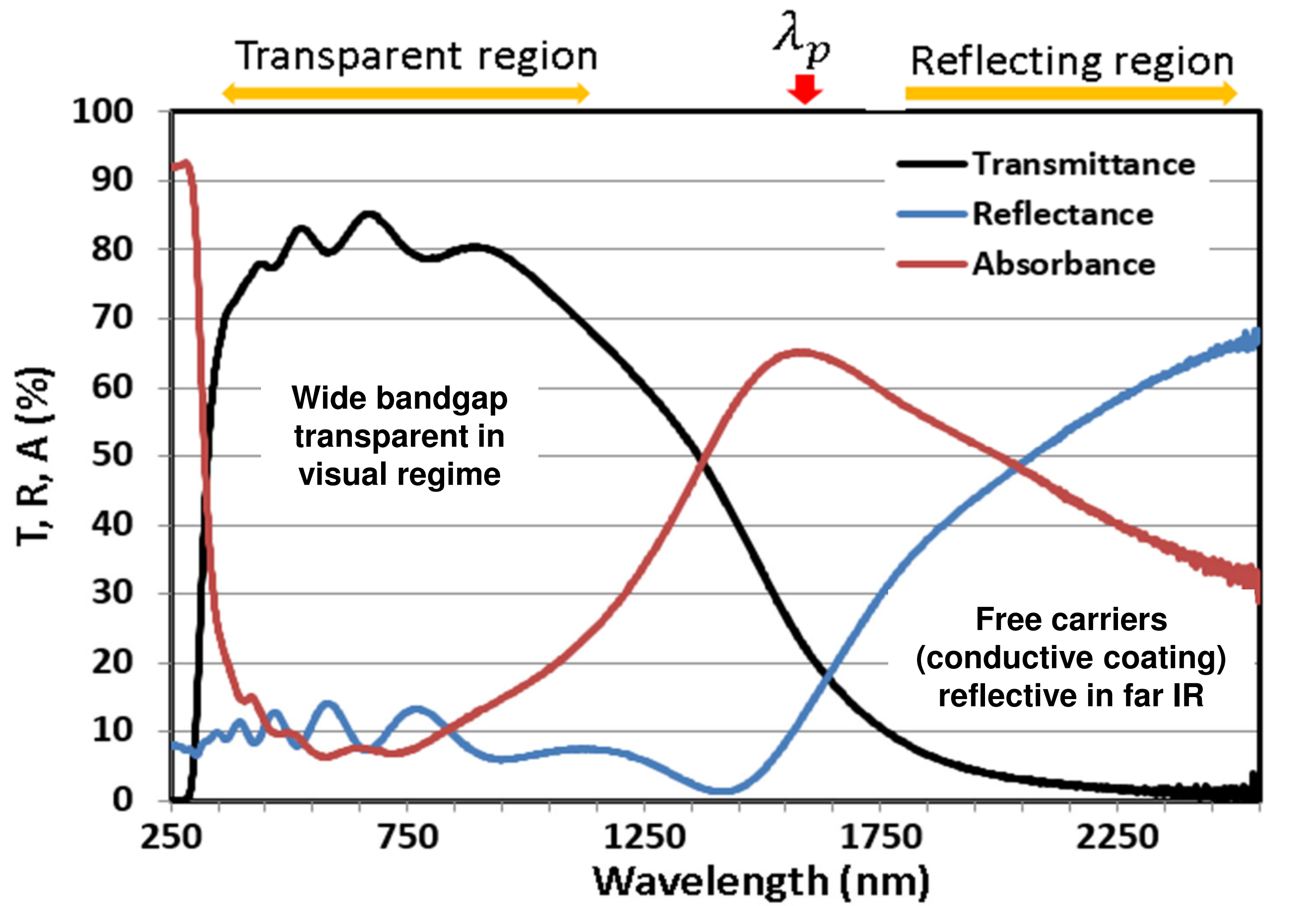


Interactions with Electromagnetic Spectrum



Materials Design – Optical Response

- **Fluorine doped SnO_2 (FTO, SnO_2:F)**



Emissivity

For an object exposed to a thermal / blackbody source

$$Absorbed\ Energy = \alpha_\lambda E_{b\lambda}(\lambda, T)$$

$$Emitted\ Energy = \varepsilon_\lambda E_{b\lambda}(\lambda, T)$$

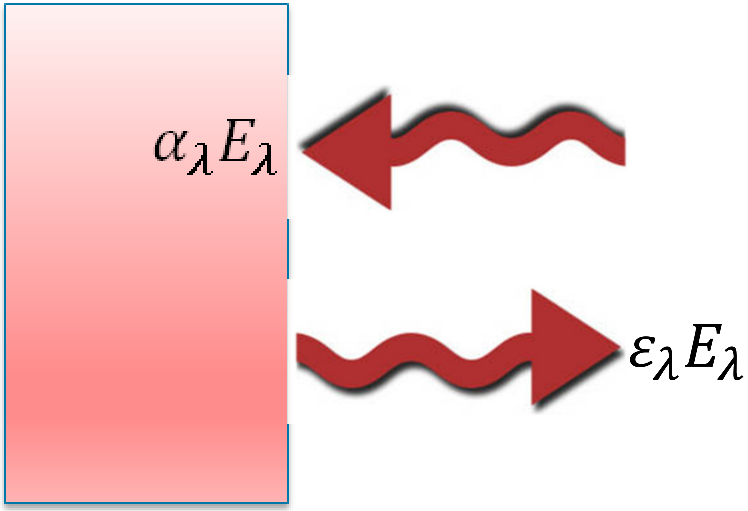
where ε_λ is the emissivity of the object at wavelength λ

Emissivity

At thermal equilibrium

$$Emitted\ Energy = Absorbed\ Energy$$

Leading to $\varepsilon_\lambda = \alpha_\lambda$ (Kirkoff's law)



Emissivity

The average emissivity then is

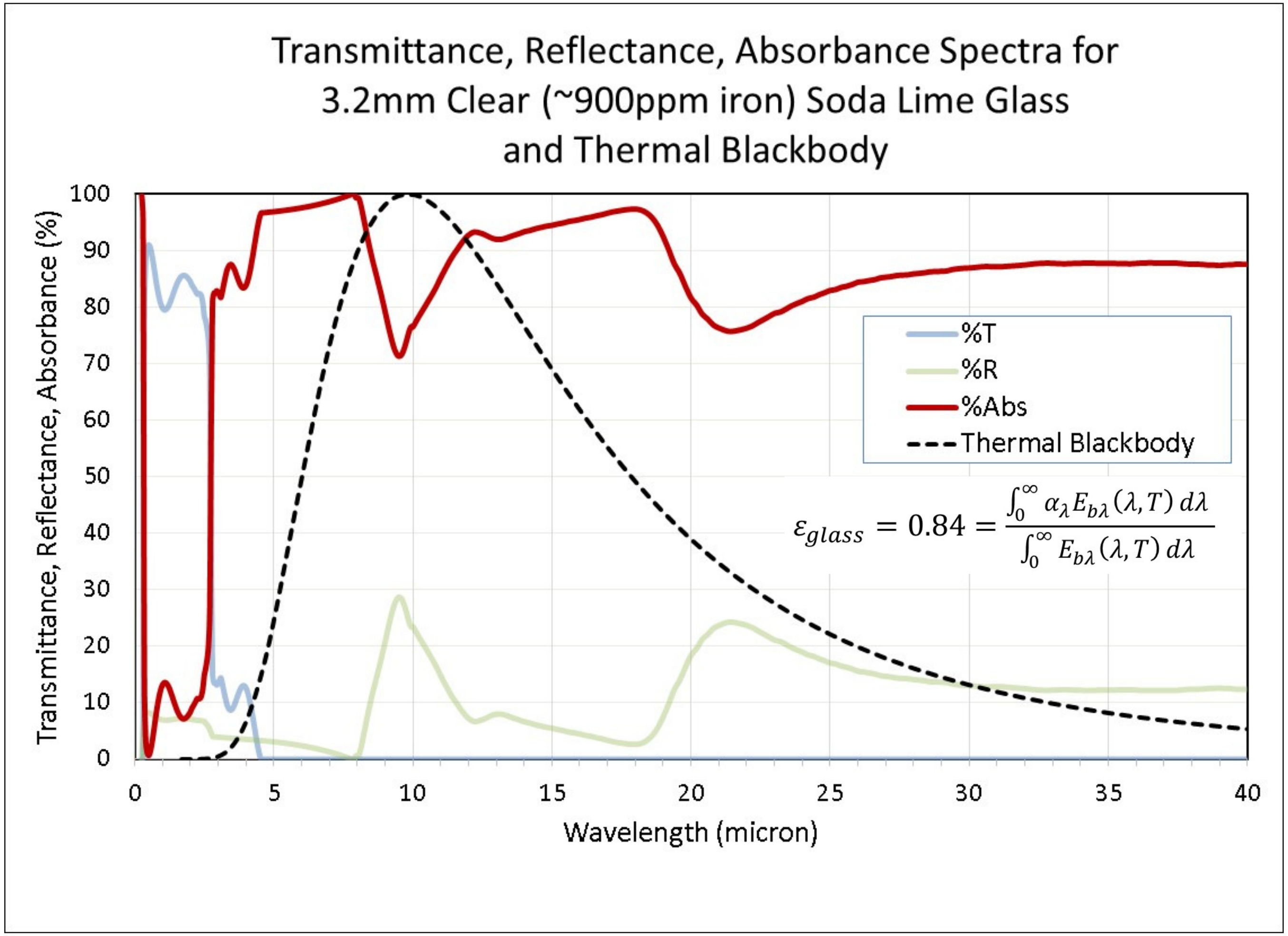
$$\bar{\varepsilon} = \frac{\int_0^\infty \varepsilon_\lambda E_{b\lambda}(\lambda, T)\, d\lambda}{\int_0^\infty E_{b\lambda}(\lambda, T)\, d\lambda}$$

Or (invoking Kirkoff's law)

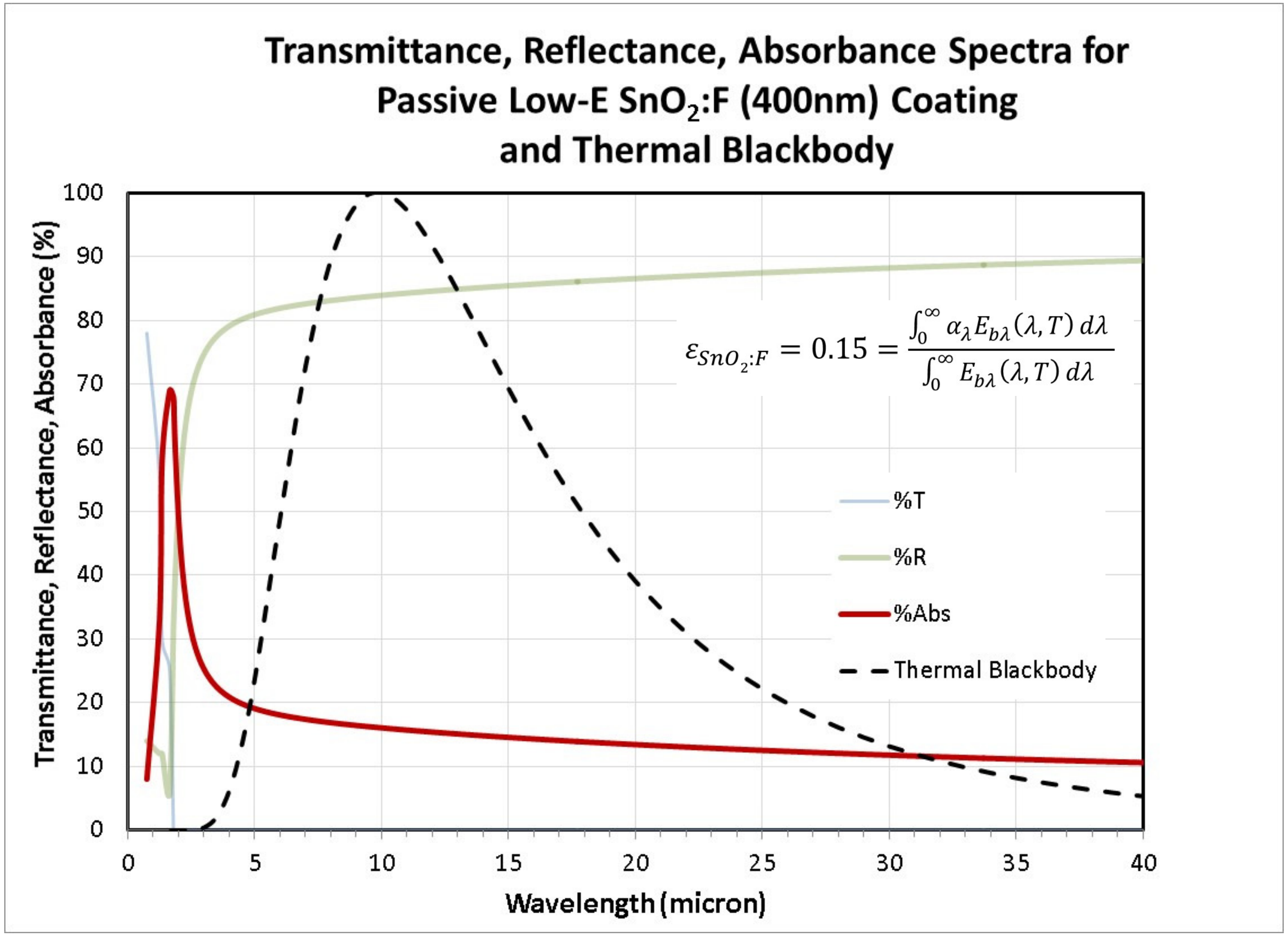
$$\bar{\varepsilon} = \frac{\int_0^\infty \alpha_\lambda E_{b\lambda}(\lambda, T)\, d\lambda}{\int_0^\infty E_{b\lambda}(\lambda, T)\, d\lambda}$$

Where α_λ is (reasonably) measurable in the lab

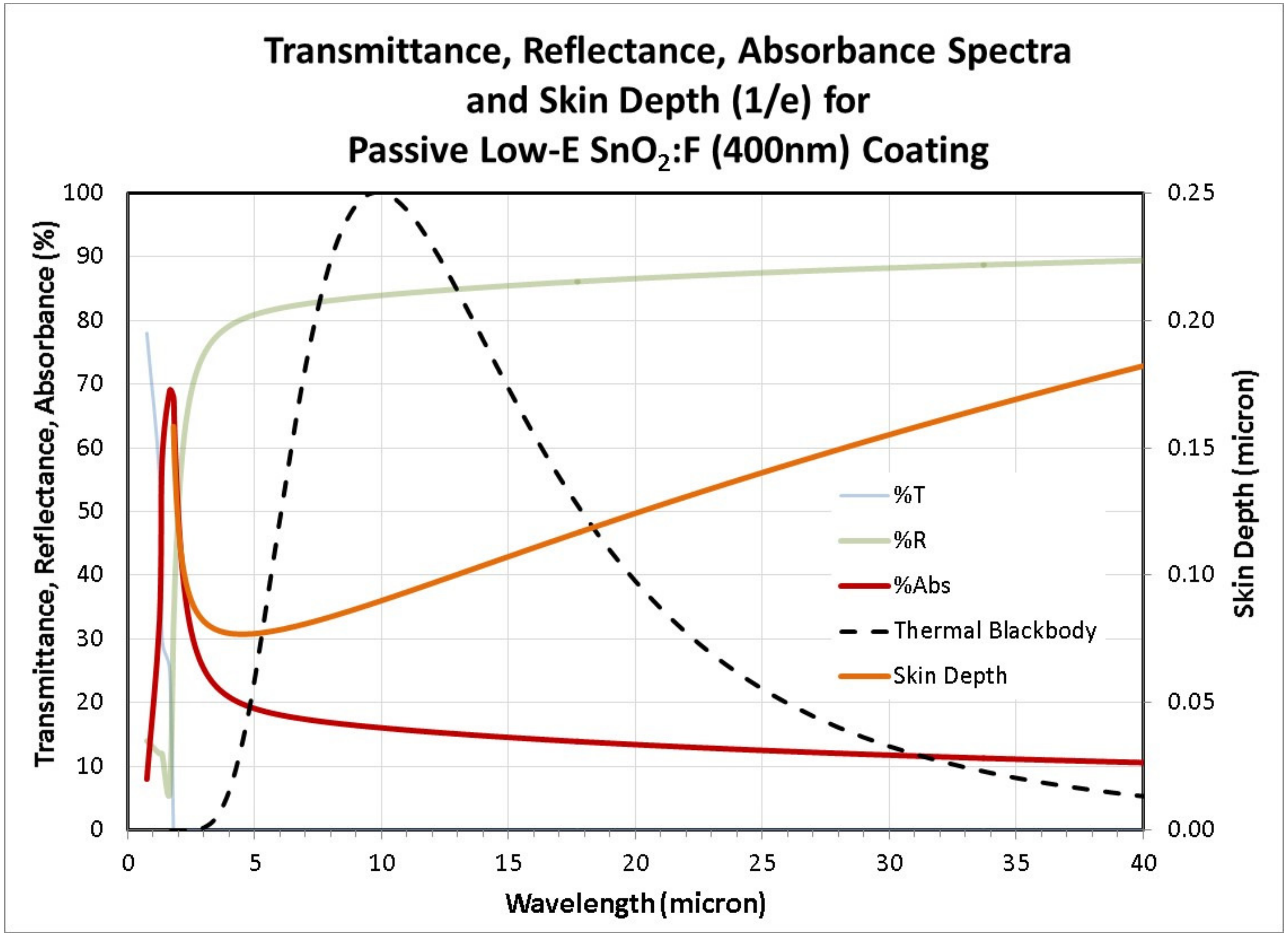
Emissivity of Uncoated Glass



Emissivity of SnO_2:F Conductive Coating

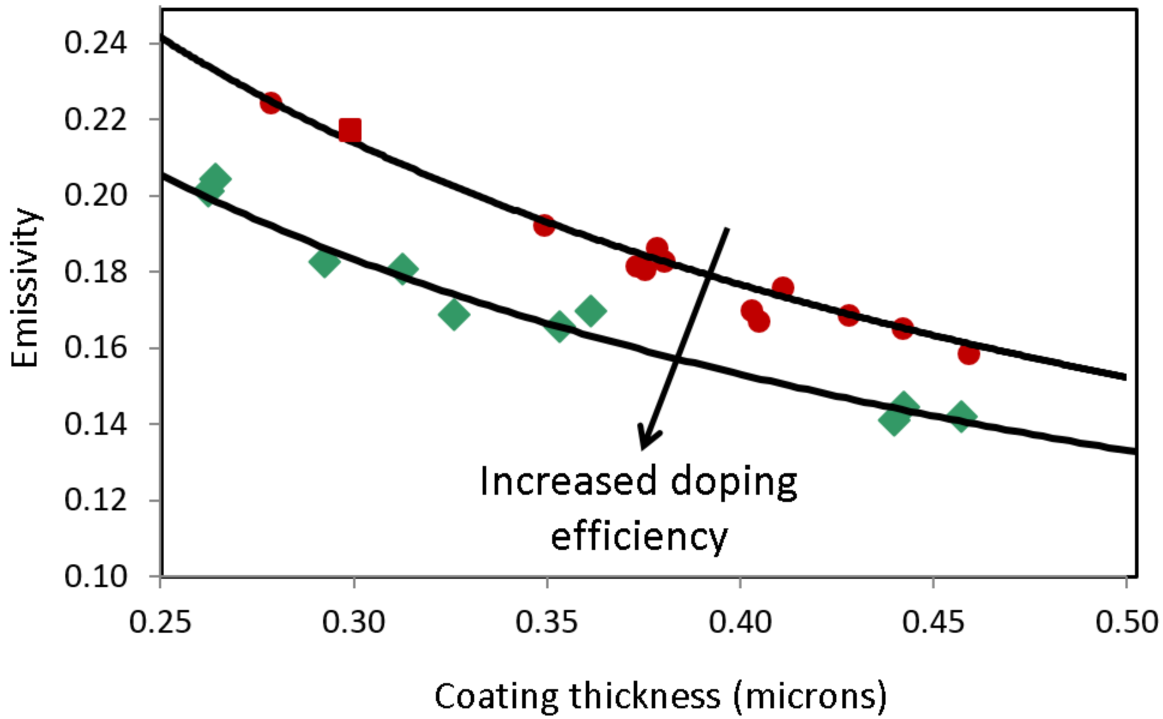


Skin Depth (1/e) of Conductive SnO_2:F Coating



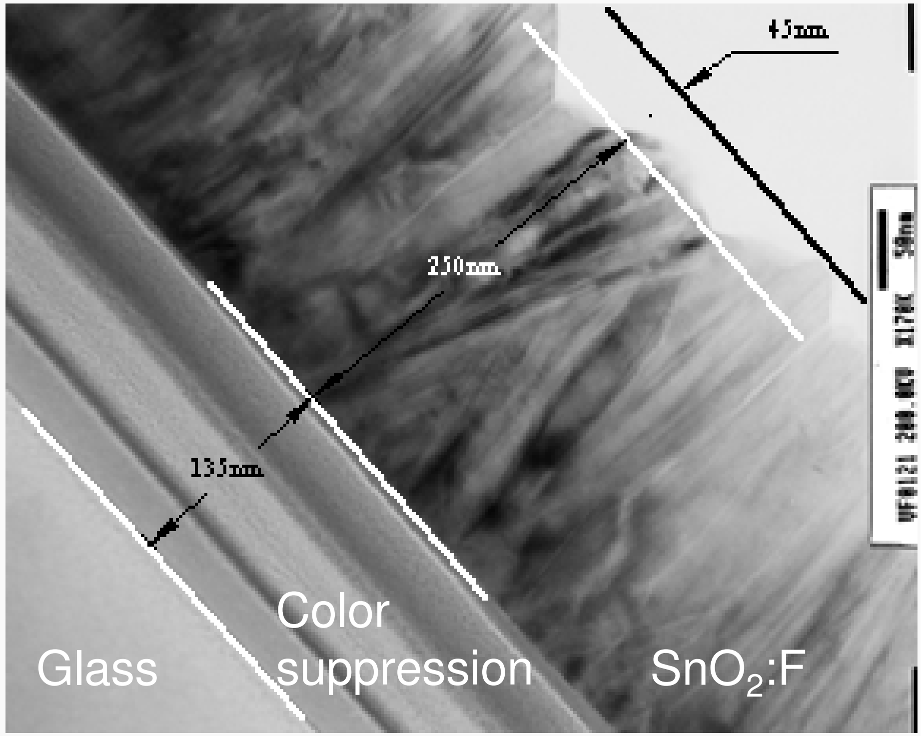
Materials and Design

- **Emissivity control**
  - Coating thickness
  - Doping efficiency



Materials and Design

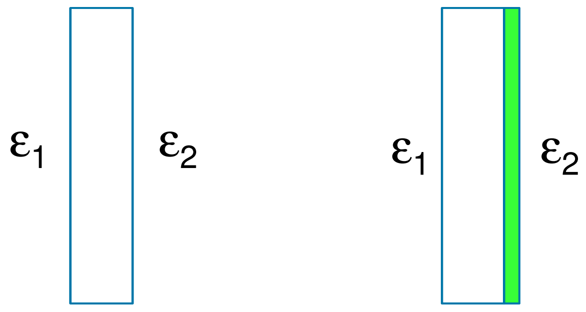
- **Growth modes**
  - Amorphous layers
    - Flat interfaces
  - Crystalline / columnar growth
    - Crystal quality improves with increased thickness
    - Increased surface roughness



Materials and Design

- **Heat transfer mechanisms**
  - Radiation transport – thermal regime

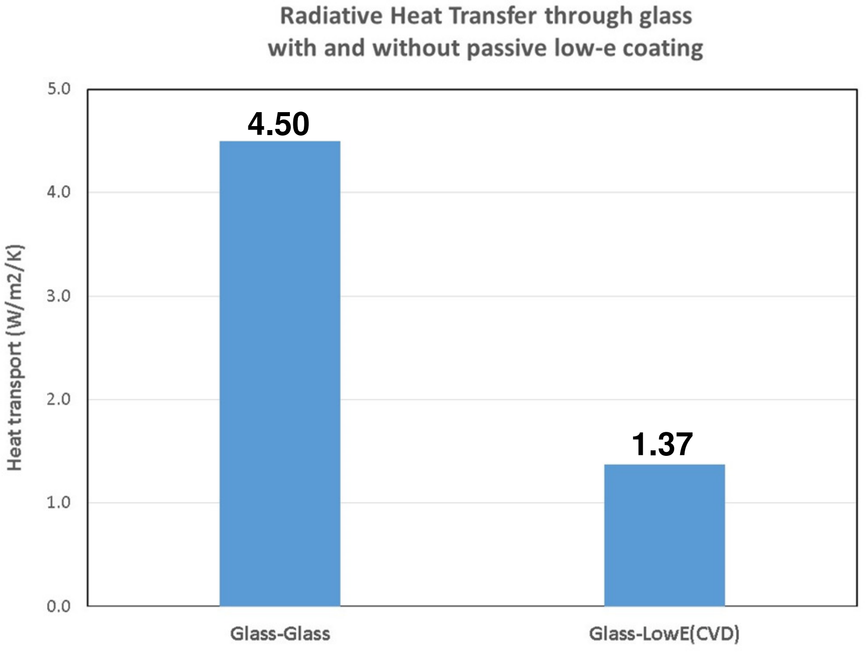
    Parallel surfaces



$$Q_{rad} = \frac{4\sigma T^3}{(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1)}$$

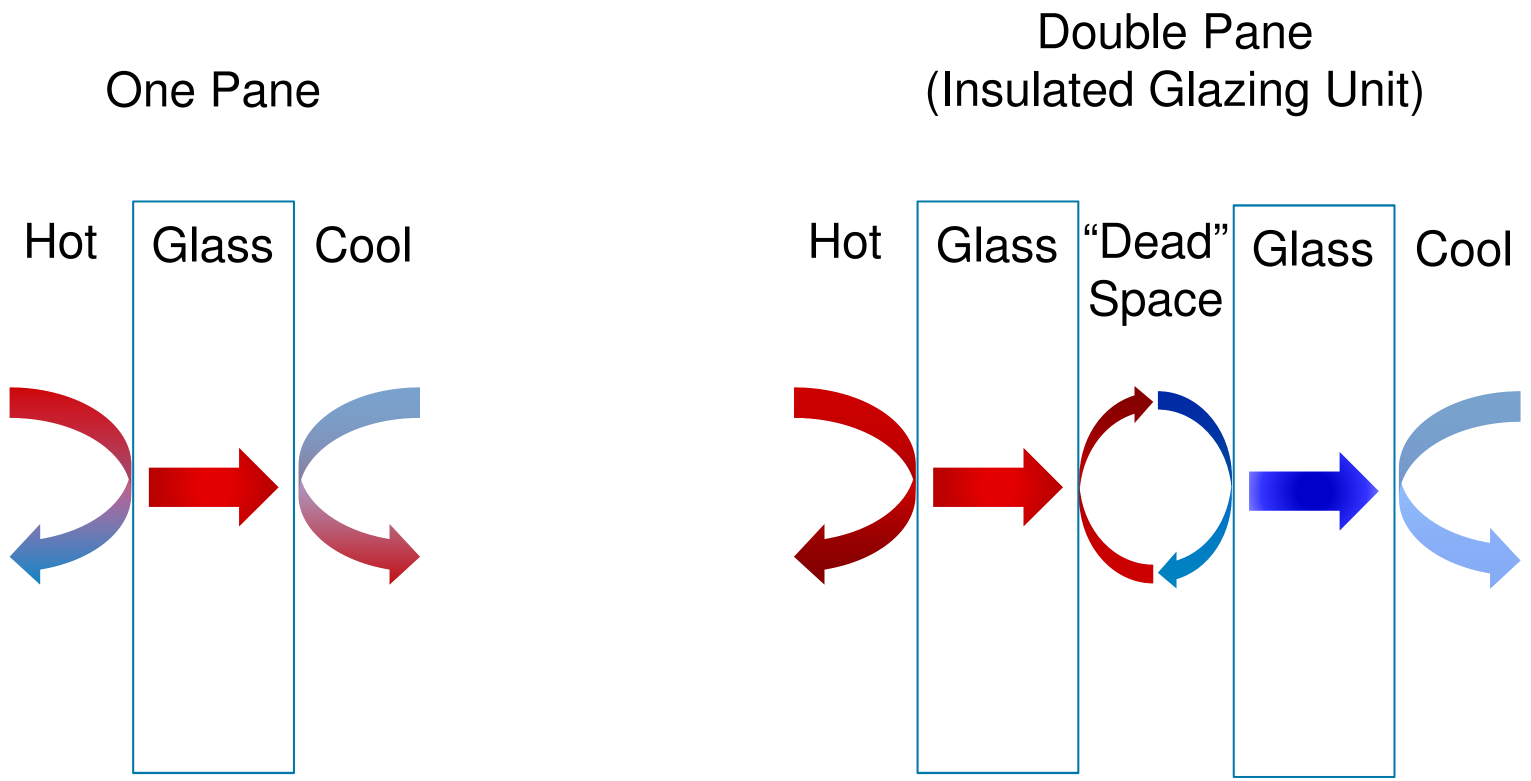
$\varepsilon_{glass} = 0.84$

$\varepsilon_{CVD} = 0.23$



Windows design for reduced heat transfer

- **Heat transfer mechanisms**
  - Convection
  - Conduction



Window Design

$$Heat\ transfer = U * A * \Delta T$$

Single pane clear glass U = 1.11

Type: Pyrolitic Low-E Clear Insulating Glass
***"Sungate®"* 500 (2) Clear + Clear** by PPG Industries, Inc.

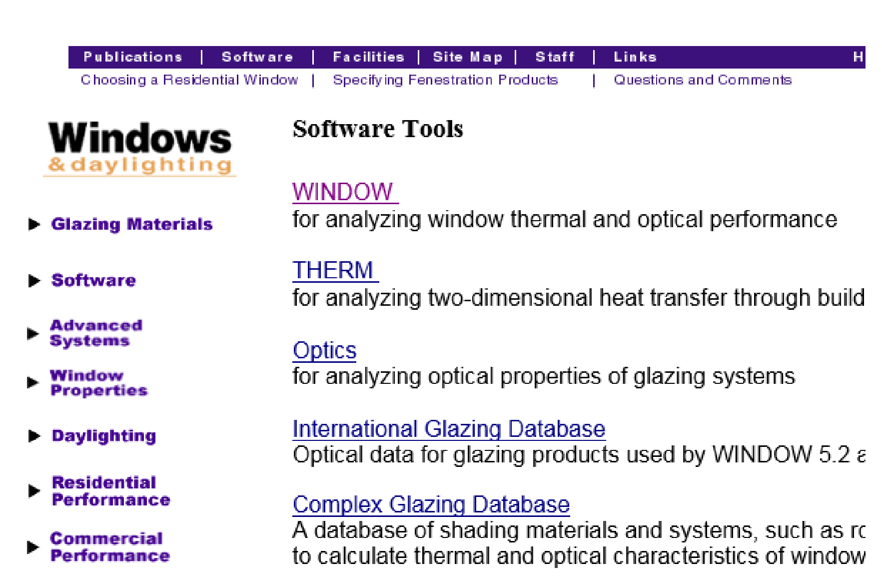
Outdoor Lite: Clear Glass, Pyrolytic Coated on second surface (2)
Indoor Lite: Clear Float Glass
Low-E Coating: ***"Sungate"*** 500 (Pyrolitic) by PPG Industries, Inc.
Location: Second Surface (2)

Performance Values

Visible Light Transmission	U-Value Winter	U-Value Summer
74%	0.35	0.35

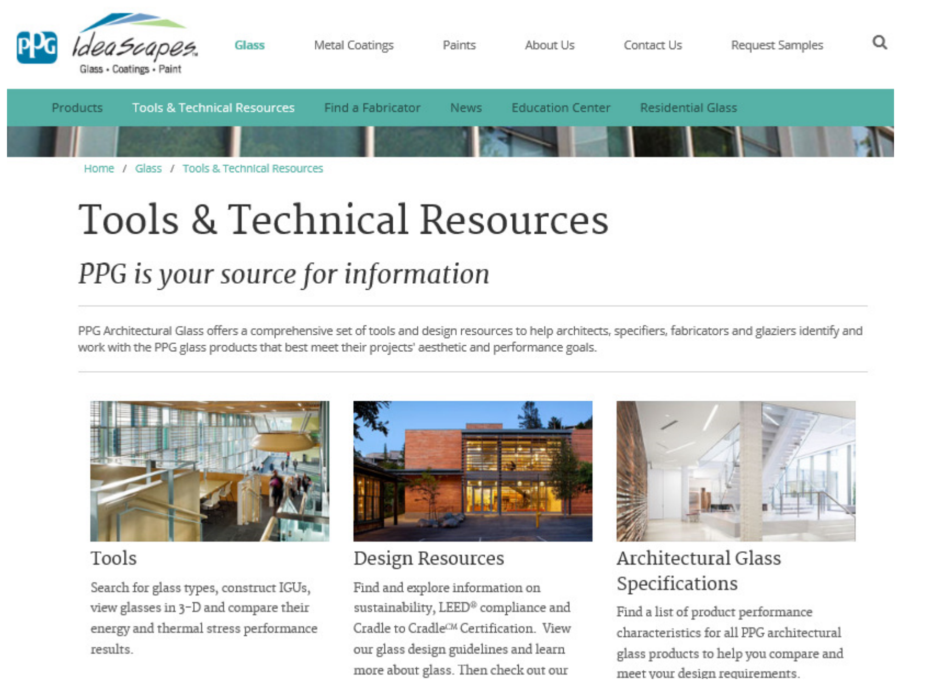
Insulating Glass Unit (IGU) window with CVD low-e coating reduces energy loss by 3X as compared with windows with single pane of glass

Window Design – resources



http://windows.lbl.gov/software/

http://www.ppgideascapes.com/Glass/Tools-Resources.aspx



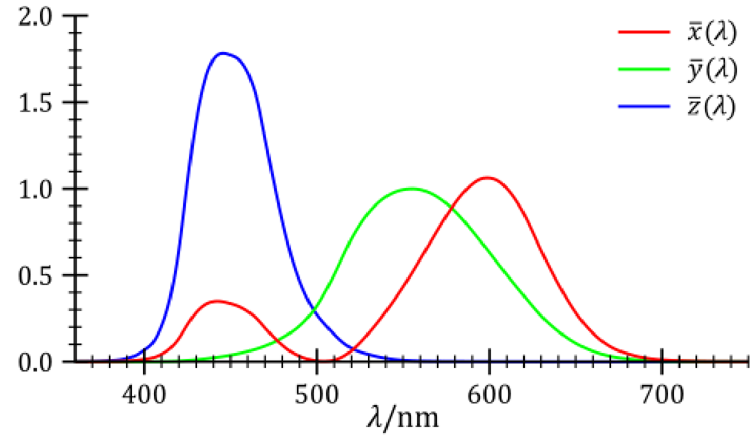
Materials and Design

- **Color can be represented in L*a*b* space**
  - Weighting functions in visual spectrum give

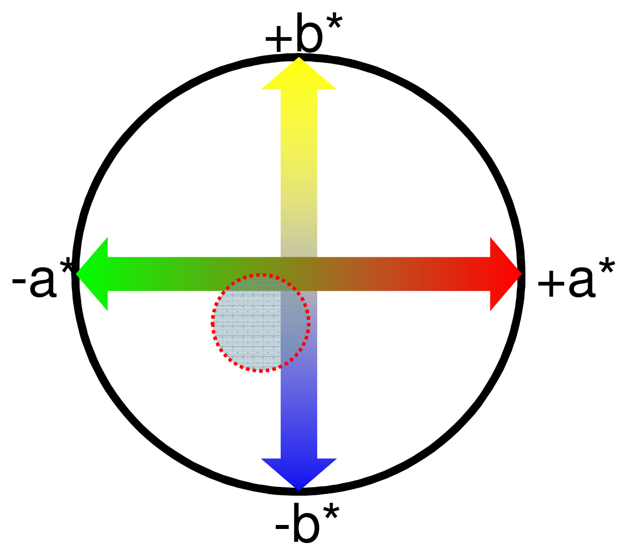
    L* - brightness

    a* - red/green axis

    b* - yellow/blue axis

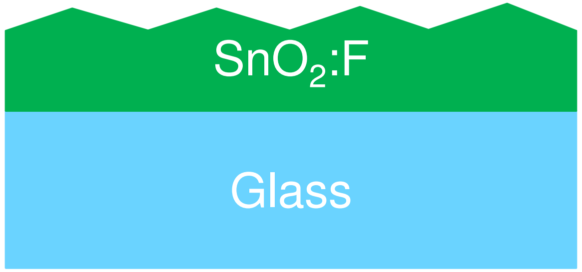


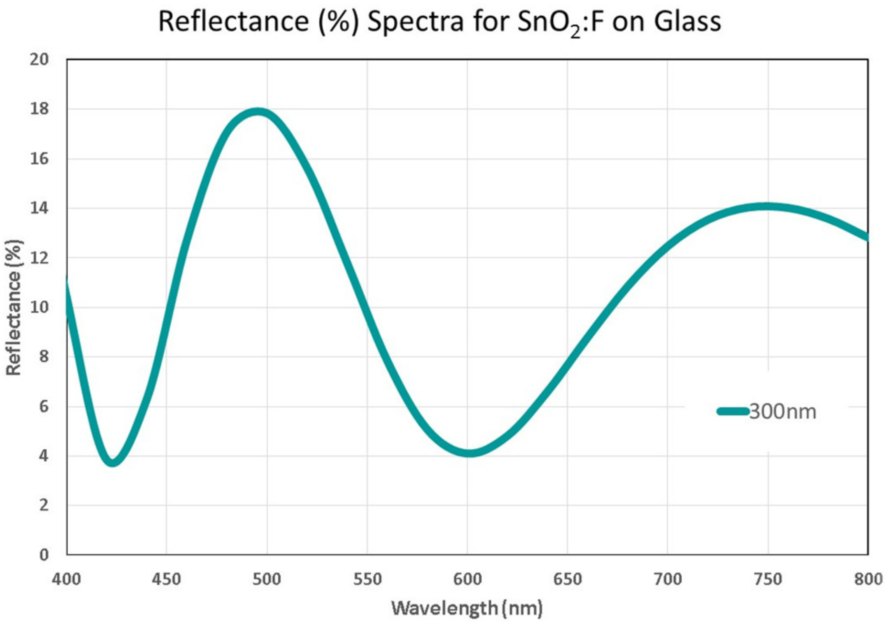
- **Customers want**
  - Neutral ~ (0,0)
  - Blue-green (-a*, -b*)

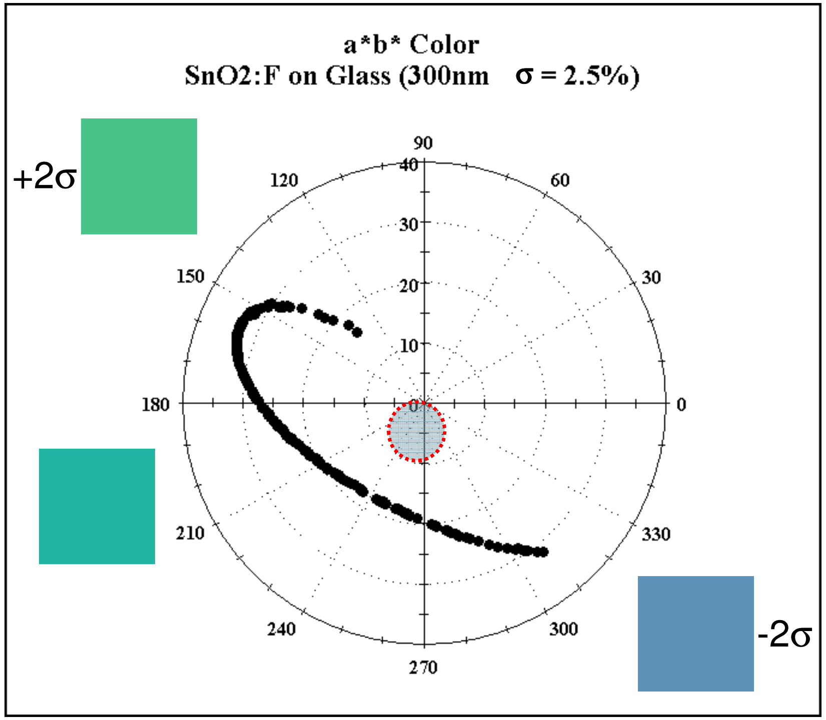


Materials and Design

- **Optical response**
  - Design of coating stack
  - Response often non-linear in color space

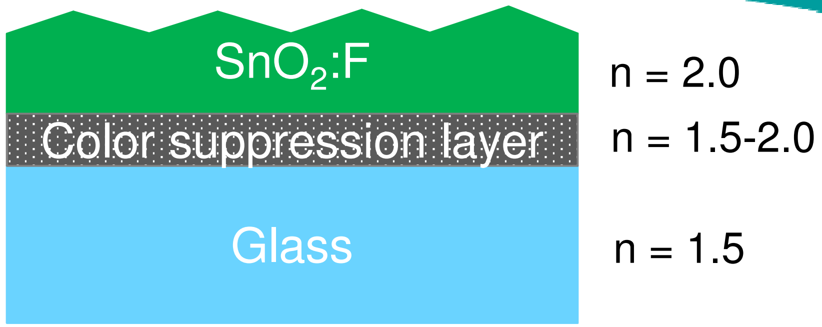


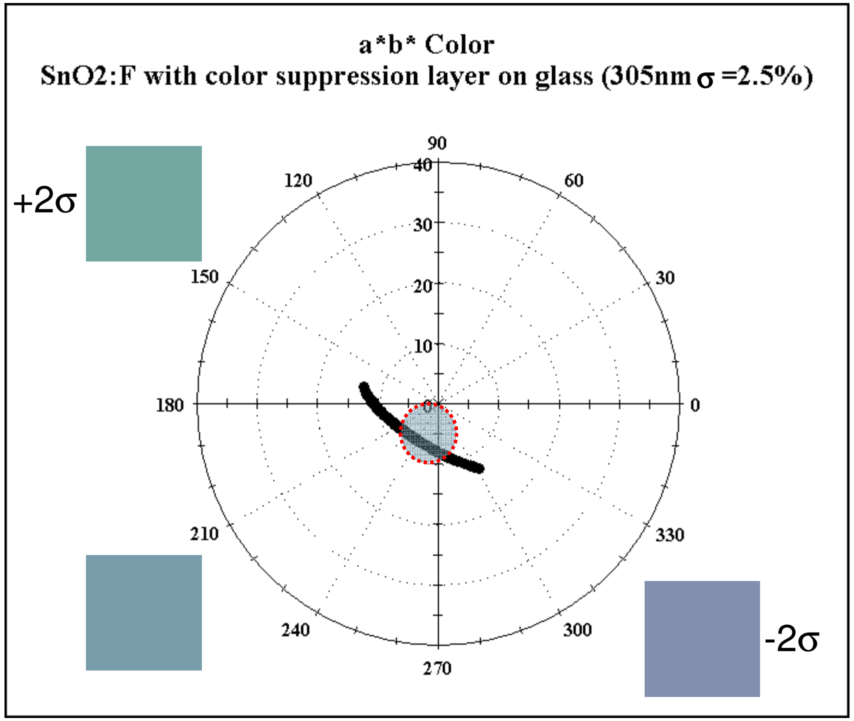




Materials and Design

- **Optical response**
  - Add color suppression layer between high index (SnO2:F) and low index (glass)





Coating Design – Color Suppression Layer

- **Color suppression layer approaches**
  - Discrete H-L index layers
    - SnO_2 / SiO_2 / SnO_2 / SiO_2
  - Homogenous intermediate index layer
    - $Si_xSn_{(1-x)}O_{(2-\delta)}C_\delta$
  - Graded optical index
    - Mixed metal oxides
    - $Si_xSn_{(1-x)}O_2$ (x is a function of layer thickness)
    - $Si_xTi_{(1-x)}O_2$ (x is a function of layer thickness)

Chemistry for CVD Coatings

- **Typical precursors** *All are unsafe if not used properly!*
  - SnO_2
    - Monobutyl tin trichloride ($C_4H_9SnCl_3$)
    - Bibutyl tin dichloride ($(CH_3CH_2CH_2CH_2)_2SnCl_2$)
    - Trimethyl tin ($C_4H_{12}Sn$)
  - F
    - Hydrofluoric acid (HF)
    - Trifluoroacetic acid ($C_2HF_3O_2$)
  - SiO_2
    - Tetraethyl orthosilicate ($SiC_8H_{20}O_4$ - TEOS)
    - Silane (SiH_4)
    - Monochlorosilane ($SiClH_3$)
  - TiO_2
    - Titanium isopropoxide ($C_{12}H_{28}O_4Ti$)
    - Titanium tetrachloride ($TiCl_4$)

Choosing a precursor – criteria to consider

- **Safety**
  - Toxic (acute, chronic exposure)
  - Flammable / pyrophoric
  - Asphyxiate (CO_2 vs N_2 vs NF_3)
- **Compatibility with other precursors**

$$2MCl_3 + 3H_2O \rightarrow 6HCl + MO_x + yO_2$$

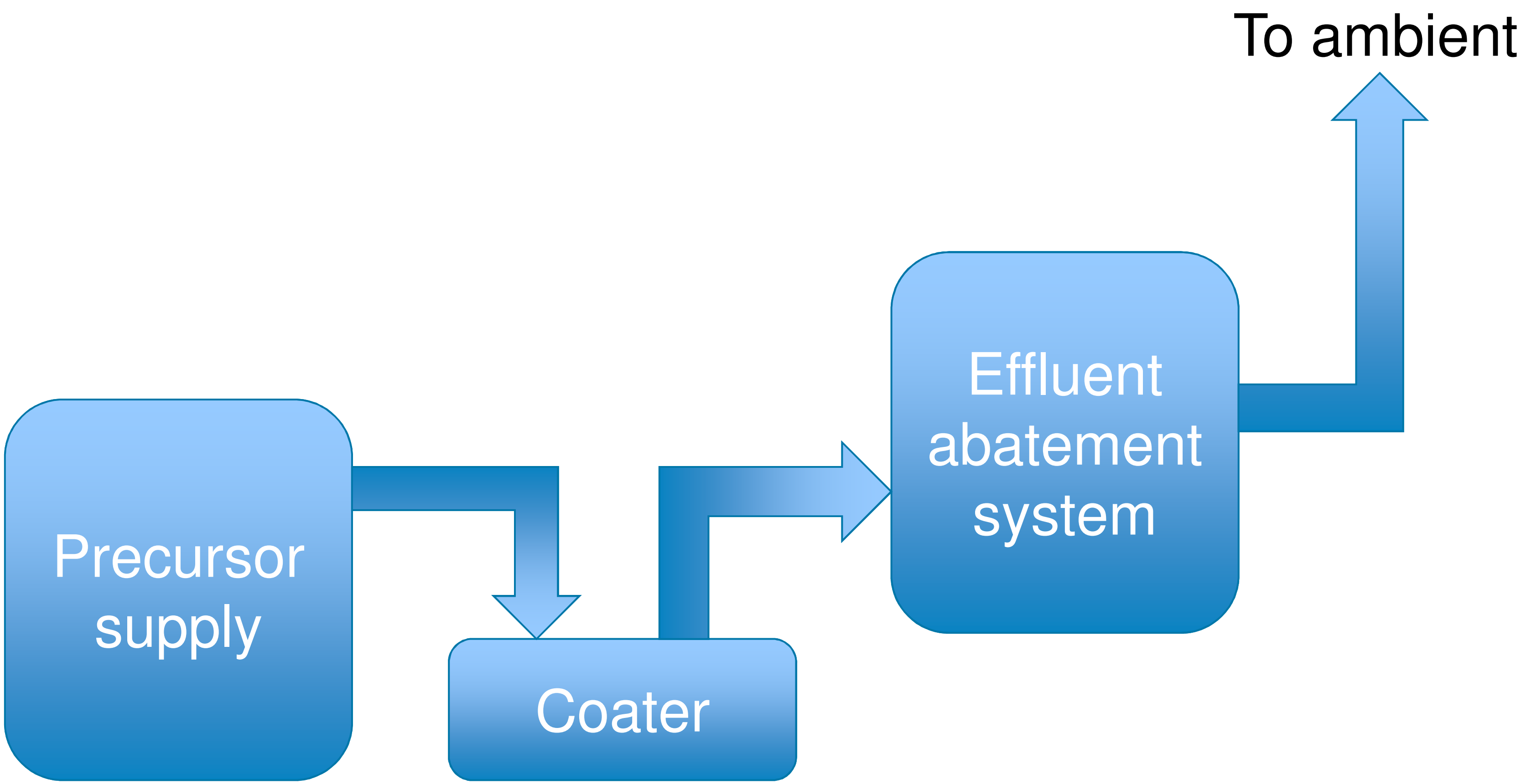
(~instantaneous, exothermic)

- **Deposition efficiency within desired / allowable temperature regime**
- **Cost**

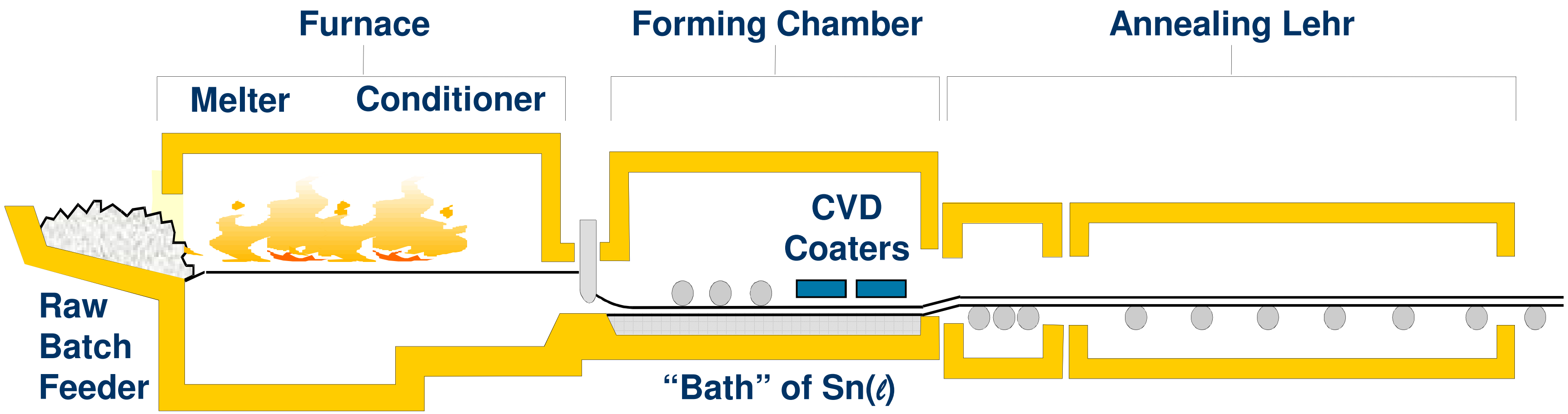
Questions

Process and Equipment

Process & Equipment – basic unit operations



Process & Equipment – coater location



- **Float glass**
  - 25 MM m²/yr per line
- **Online CVD coating**
  - 10 MM m²/yr per line
- **Efficient use of energy**
  - Use existing energy content of the glass

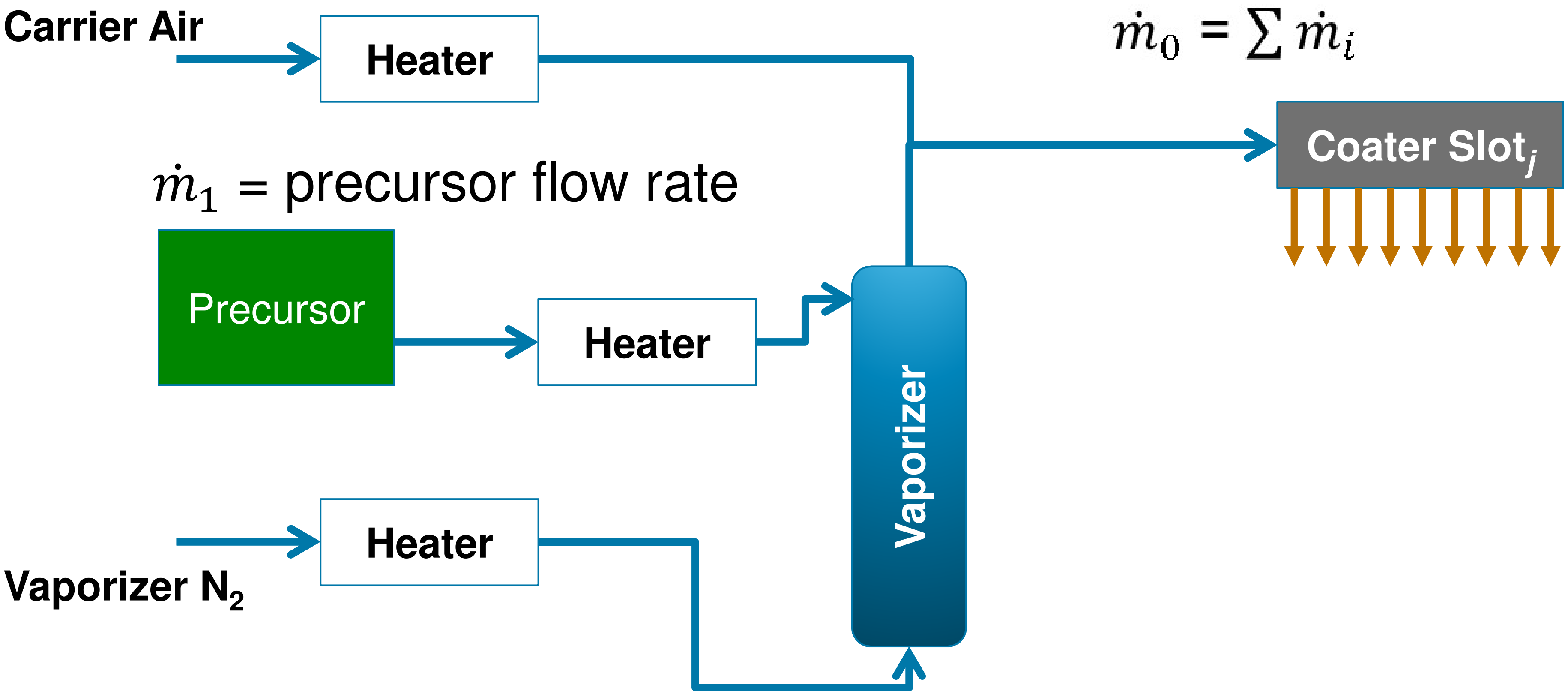
- Glass Temperature = 600-675°C
- Glass Speed = 5 to 15 meters/min.

Precursor flow system

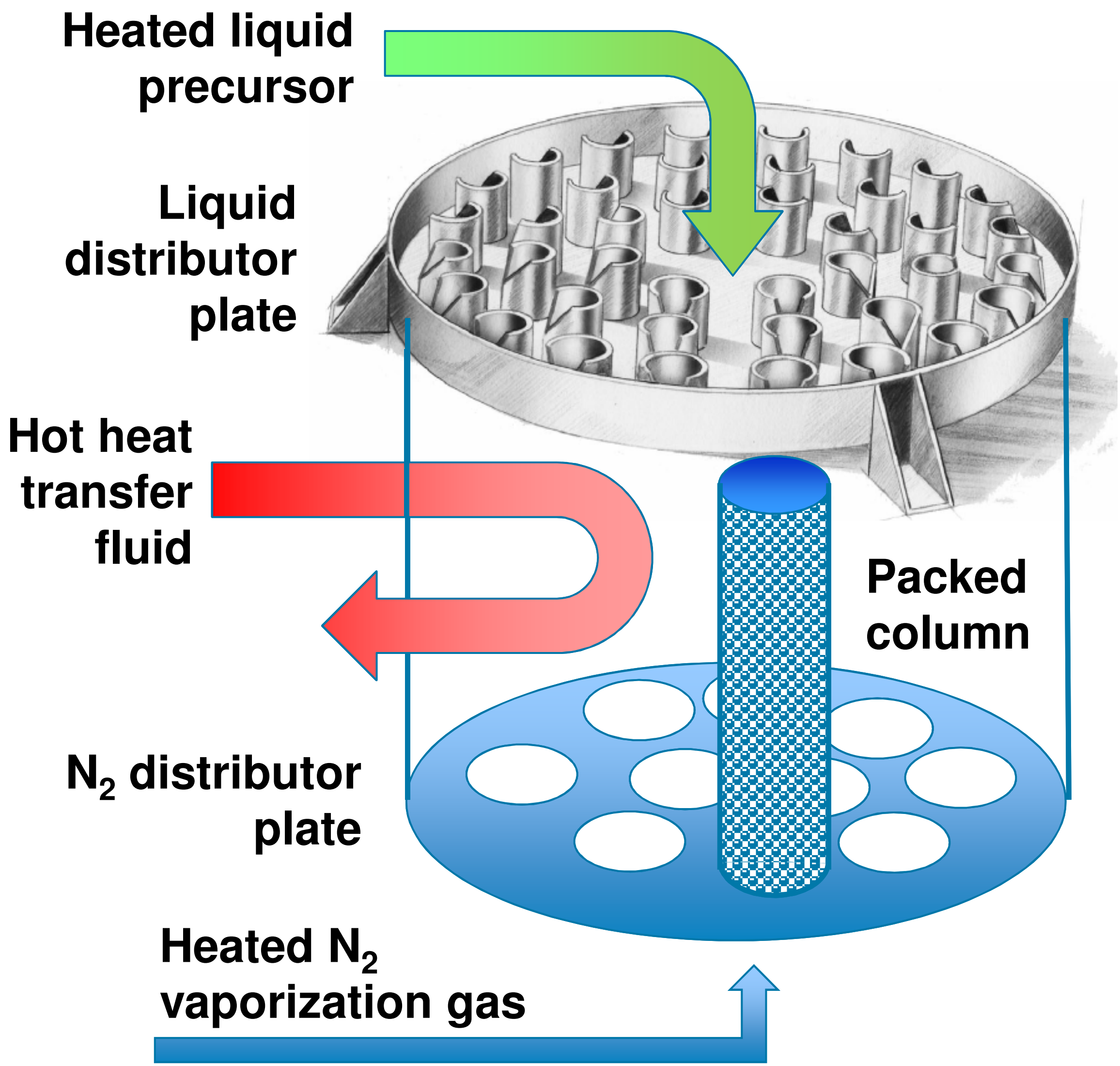
$\dot{m}_0$ = total flow rate

$\dot{m}_0 = \sum \dot{m}_i$

$\dot{m}_1$ = precursor flow rate

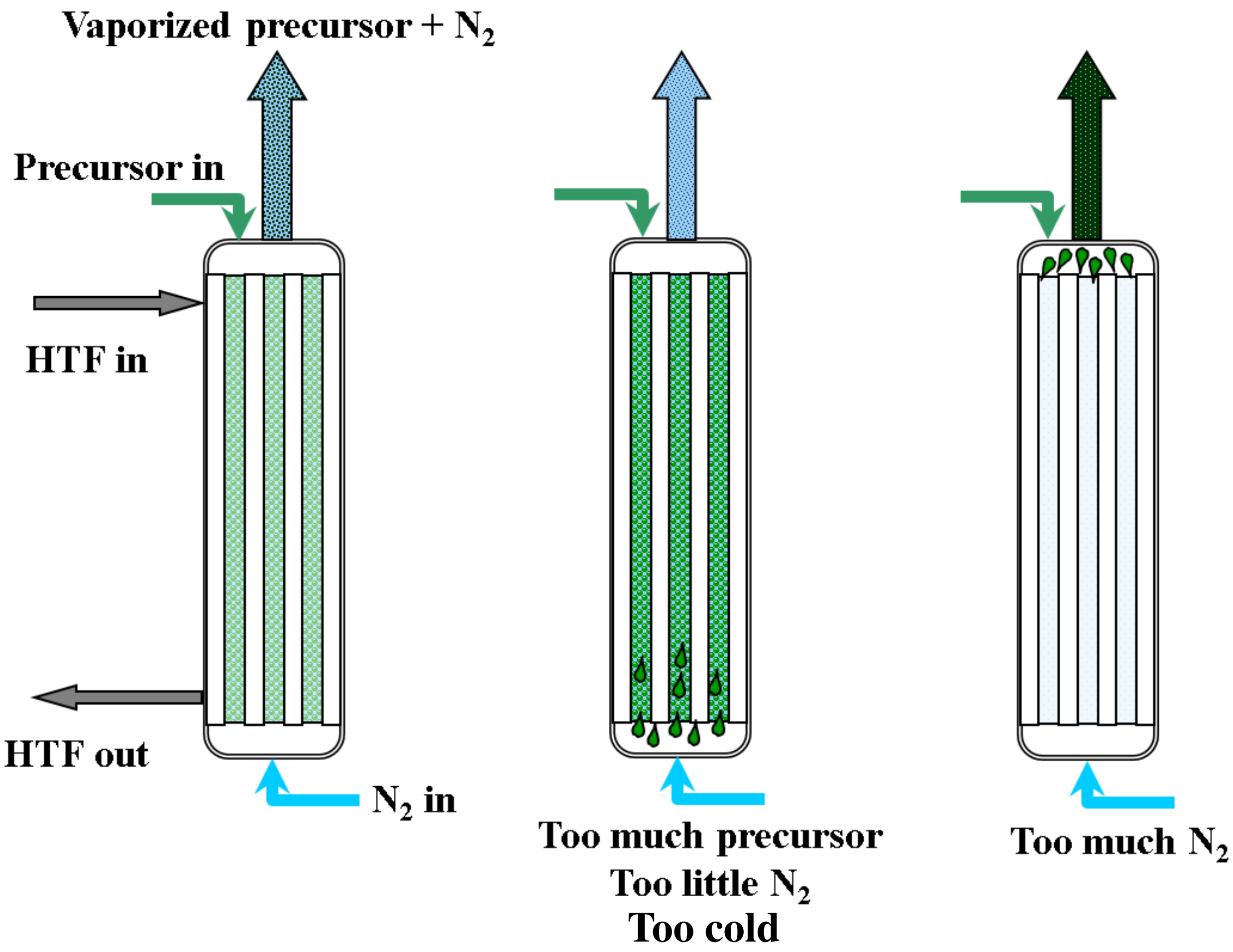


Process & Equipment – precursor vaporization



- **Liquid distributor fouling resistance (best to worst)**
  - V-notch weir
  - Spray
  - Slotted weir
  - Sidewall orifice
- **Packing types**
  - Metal chips
  - Raschig rings
  - Pall rings

Process & Equipment – vaporizer operations



3 potential operating conditions

Process & Equipment – vaporizer operation

- **What is the operating temperature for vaporization of MBTC**
  - 36.5 lb/hr MBTC flow
  - 20 SCFM N_2

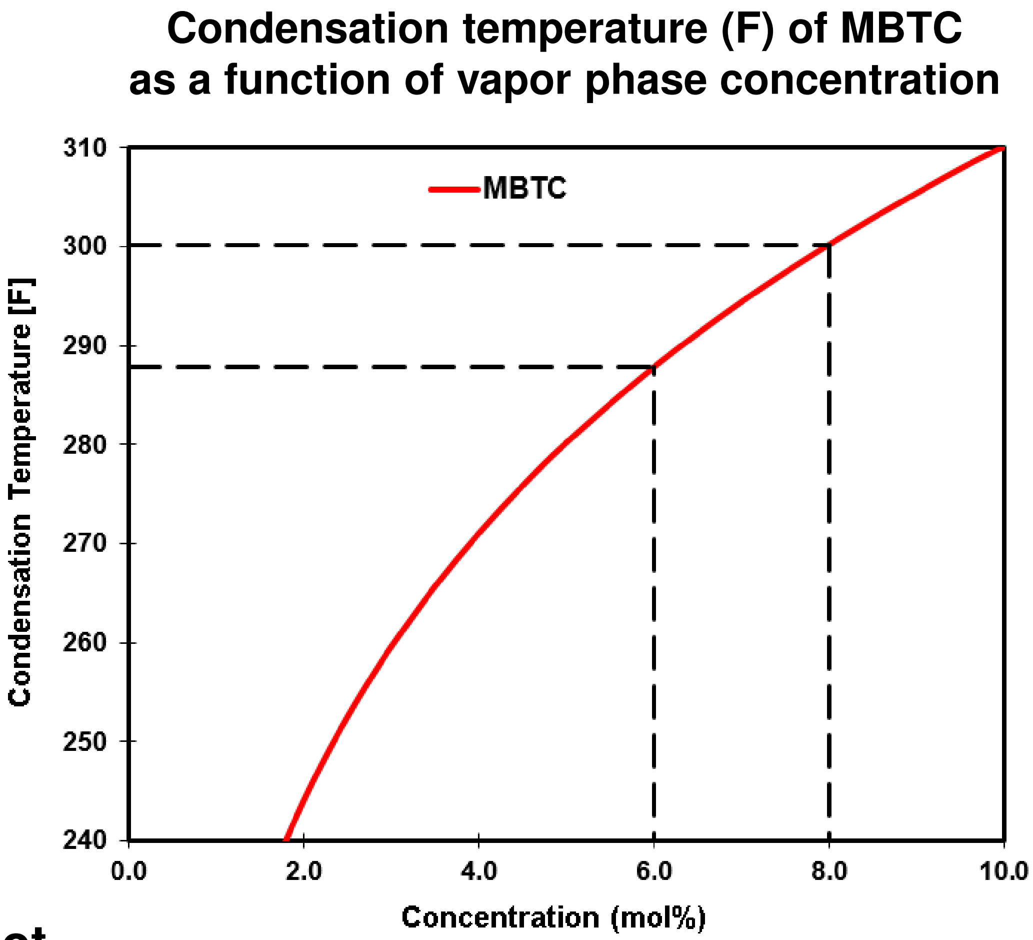
MW_{MBTC} = 282 lb / lb-mol

N_2 std vol = 386.7 SCF / lb-mol

MBTC concentration = 4%

T_{op} > 271 F

If T_{op} < 270F expect liquid into pot



Process & Equipment – vaporizer operation

- **Souder-Brown equation predicts entrainment when velocity V in the vaporizer packed column is greater than V_G**

Souder-Brown Eqn.

$$V_G = k\sqrt{\frac{\rho_L - \rho_G}{\rho_G}}$$

For packed column
k = 0.175 ft/s

54.75 lb/hr MBTC 30 SCFM N_2 T=300 F

ρ_{MBTC} = 91.95 lb/ft^3 ρ_{vap} = 0.0531 lb/ft^3

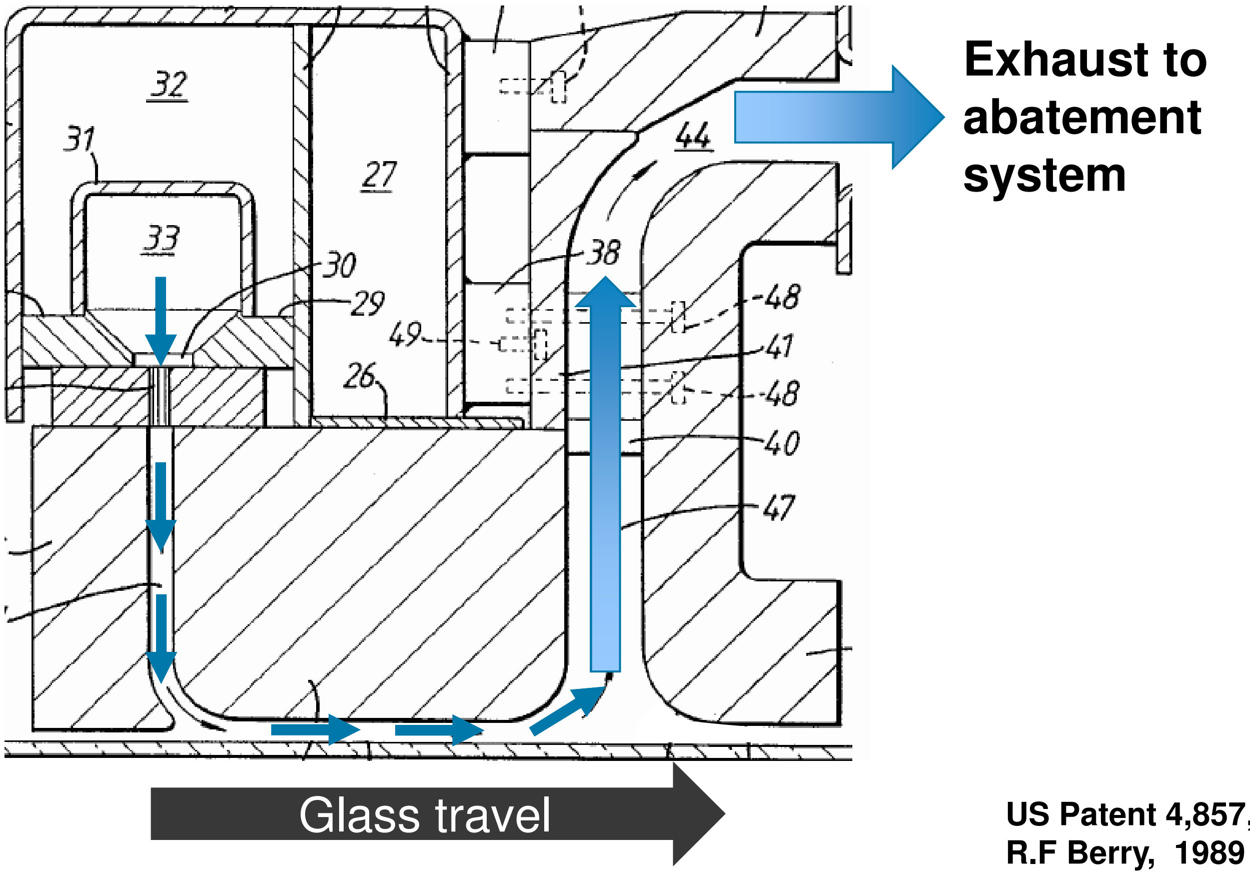
12 tubes (1-1/4" sch 10) ID = 1.442"

$V_{vap+chem}$ = 5.49 ft/s V_G = 4.93 ft/s

Entrainment is expected → "coater drip"

Process & Equipment – basic coater design

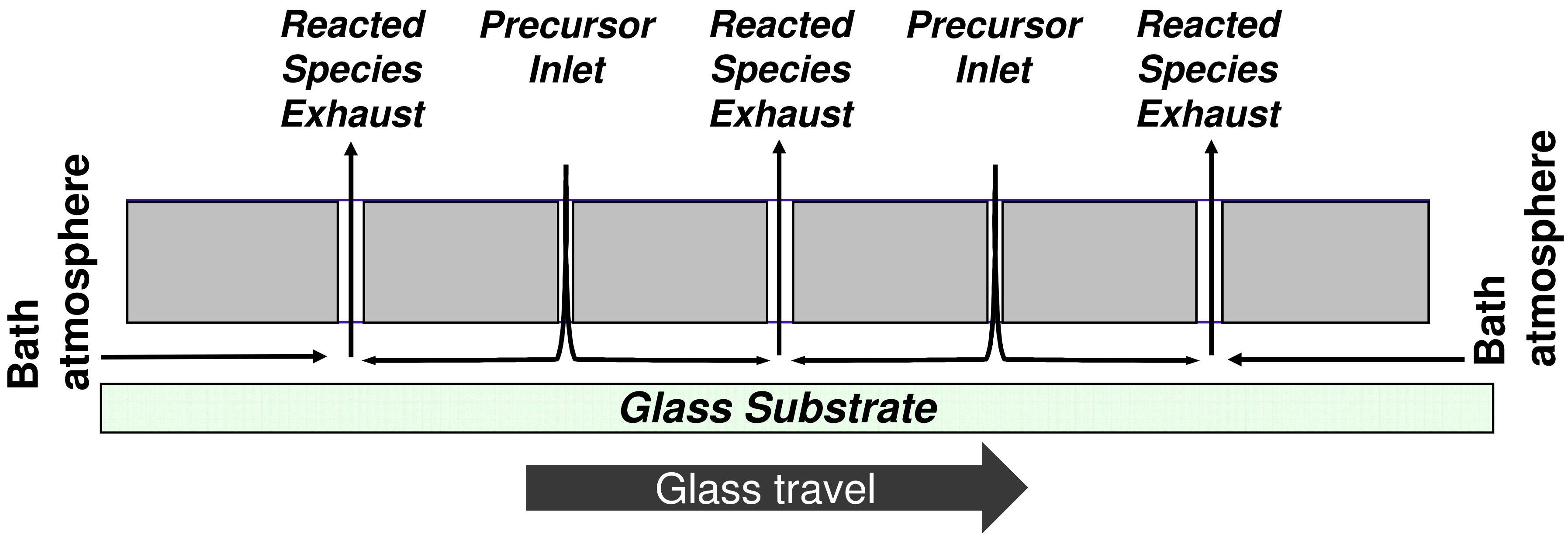
- Single inlet and exhaust



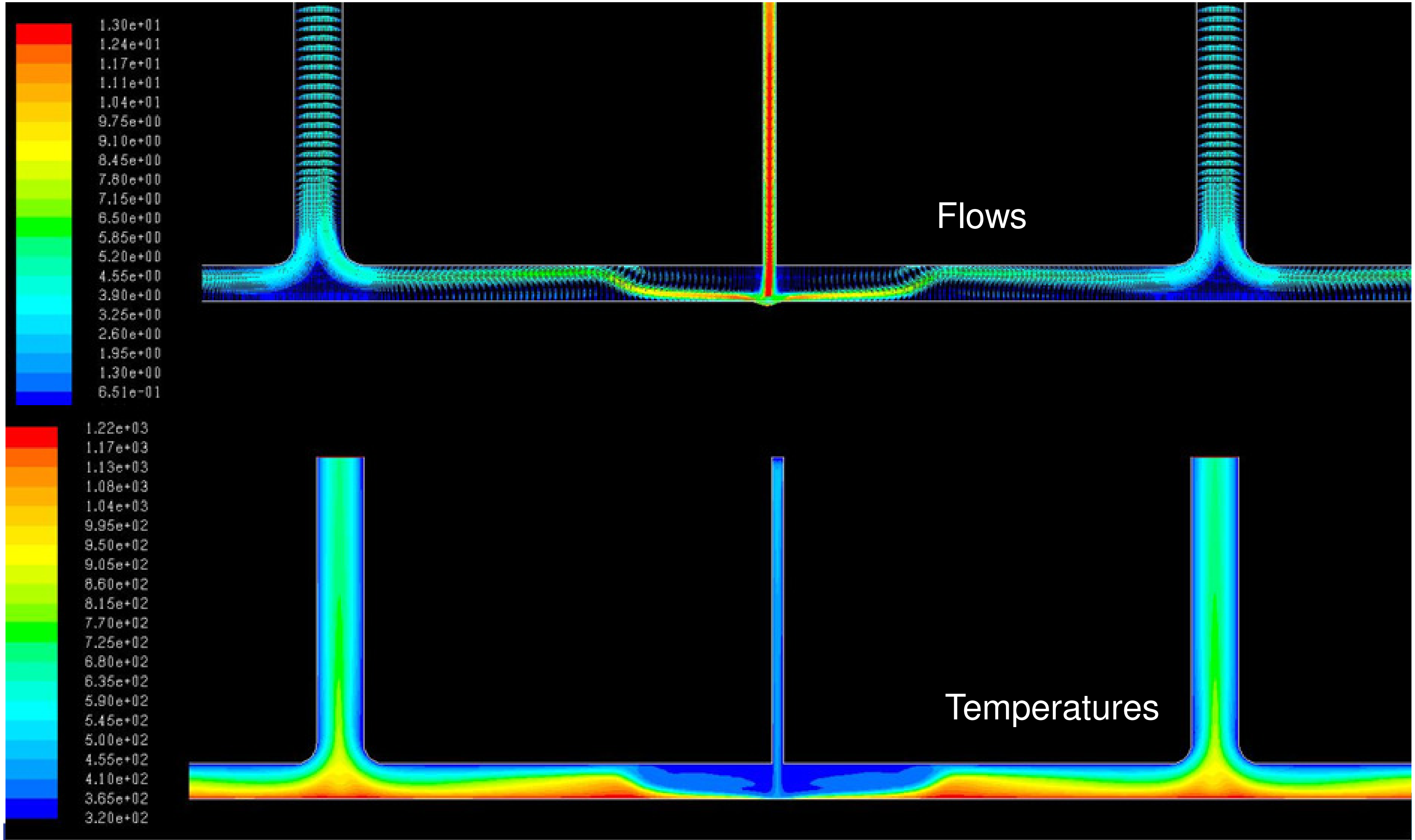
US Patent 4,857,097
R.F Berry, 1989

Process & Equipment – basic coater design

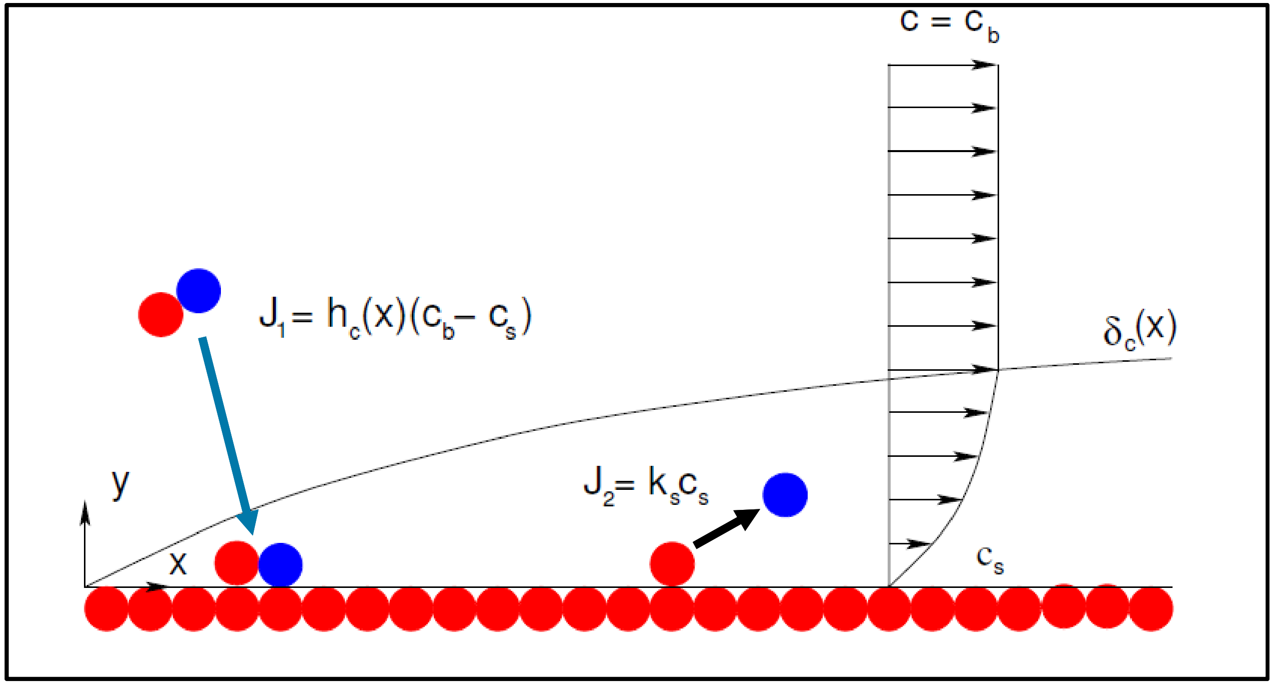
- **Inlet paired with 2 exhausts with flows both upstream & downstream**



Flows and temperatures under coater



Deposition mechanism



$$J = \frac{c_g}{\delta / D + 1 / k_s}$$

2 mechanisms: (1) mass transport, (2) reaction at surface

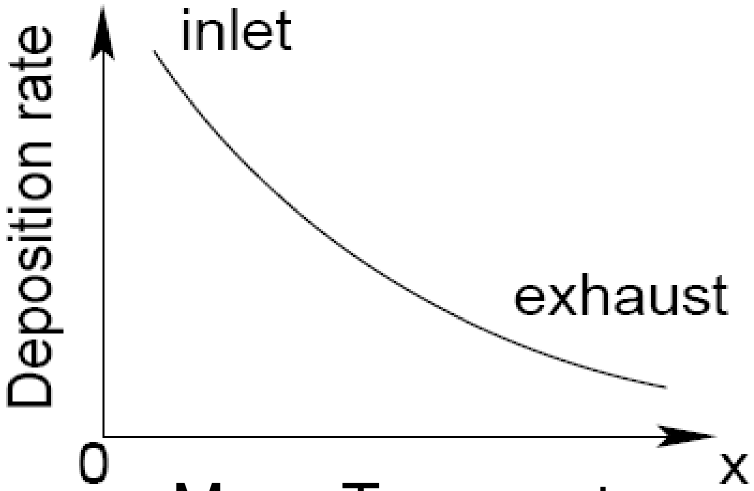
Deposition Mechanism

$$J = \frac{C_g}{\delta / D}$$

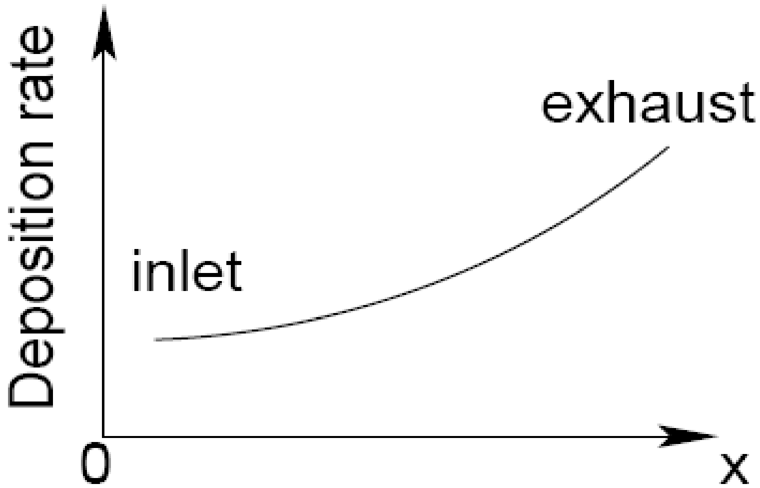
$$\delta(x) \propto \sqrt{x/u}$$

$$J = C_g k_s = C_g e^{-E/kT}$$

$$T = F(x)$$



Mass Transport Controlled



Reaction Controlled

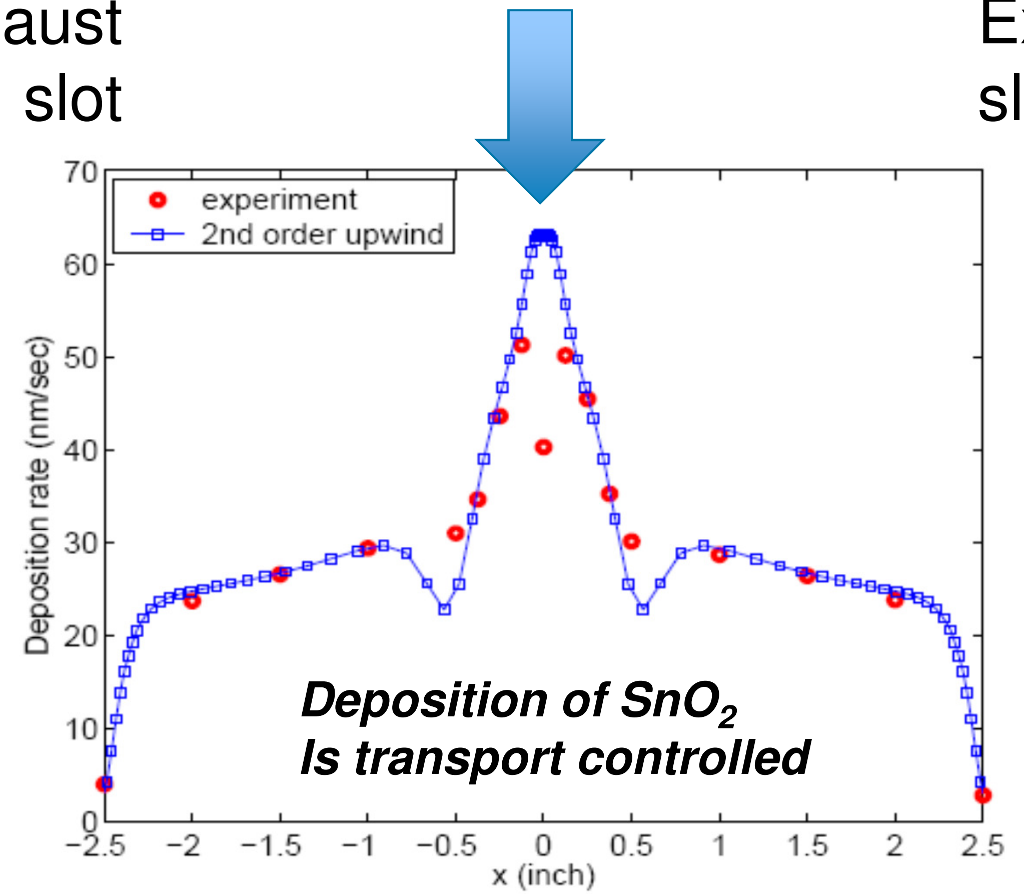
SnO_2 deposition from MBTC

Stationary glass experiment

Exhaust slot

Inlet slot

Exhaust slot

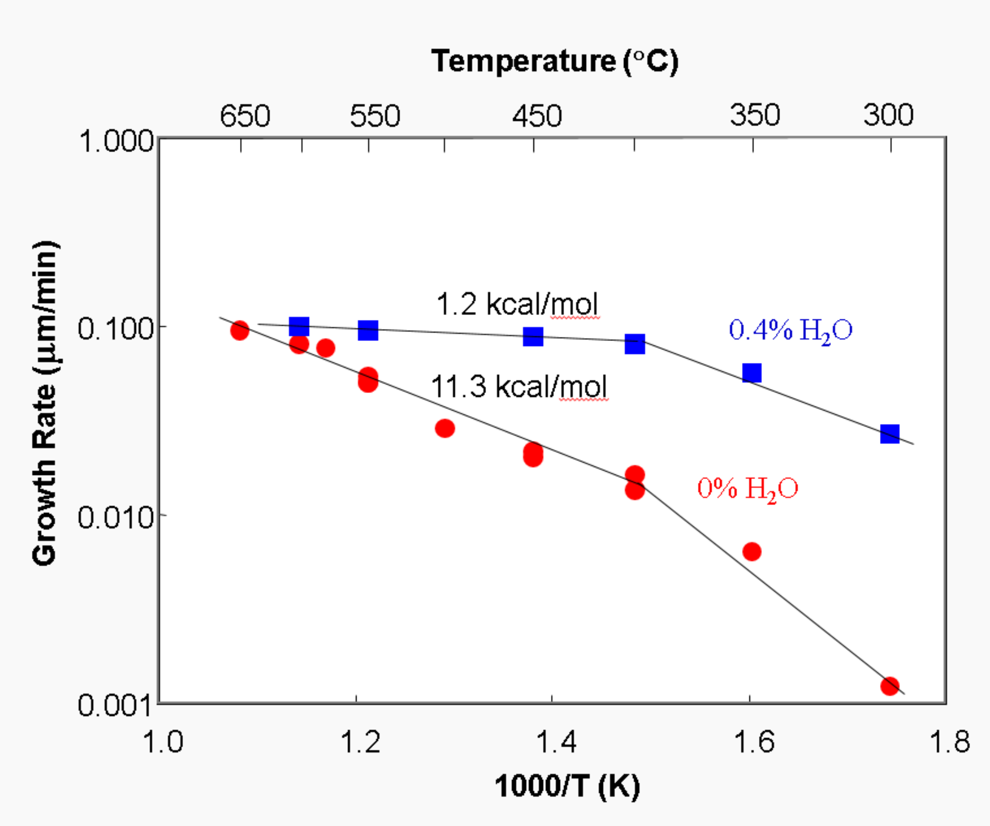


Addition of H_2O to precursor stream

- **Stagnate flow reactor experiments**
  (PPG & LBNL studies)

- **Change from reaction control to transport control for T > 375C**

- **Addition of H_2O accelerates the reaction**



Deposition mechanism – mass transport

- **For N slots with**

  L = the length between inlet and exhaust

  u = velocity of vapor

  x = distance from inlet

  ν = velocity of glass

  C_g = concentration of chemistry far from the surface

We can write for the coating thickness *h*

$$h \propto \frac{N \int_0^L \left(c_g \sqrt{\frac{u}{x}} \right) dx}{v} \propto \frac{N \cdot c_g \cdot u^{1/2} \cdot L^{1/2}}{v}$$

Deposition mechanism – mass transport

But

$$u \propto \frac{\dot{m}_0}{N \cdot H}$$

$$c_g \propto \frac{\dot{m}_1}{\dot{m}_0}$$

Where

$\dot{m}_0$ = total mass flow rate (precursor + carrier gas)

$\dot{m}_1$ = precursor flow rate

H = coater height above the glass

Such that…

$$h \propto \sqrt{N \cdot L} \cdot \frac{\dot{m}_1}{\sqrt{\dot{m}_0}} \cdot \frac{1}{\sqrt{H}} \cdot \frac{1}{v}$$

Deposition mechanism – mass transport

Similar to the mass transport case

$$J = C_g e^{-E/kT}$$

$$h \propto \frac{\dot{m}_1}{\dot{m}_0} \frac{e^{-E/kT}}{T} \frac{L}{\nu}$$

Materials and Design

- **Low maintenance coatings ("self cleaning")**
  - TiO_2
  - Low surface energy when clean – hydrophilic
  - Wide bandgap semiconductor – produces e-h pairs with UV

Same deposition mechanism as SnO_2?

Design of Experiments – ask what controls thickness

- **Mass transport controlled**
- **Reaction controlled**

$$\frac{\dot{m}_1}{\sqrt{\dot{m}_0}} \cdot \frac{1}{\sqrt{H}} \cdot \frac{\sqrt{T}}{v}$$

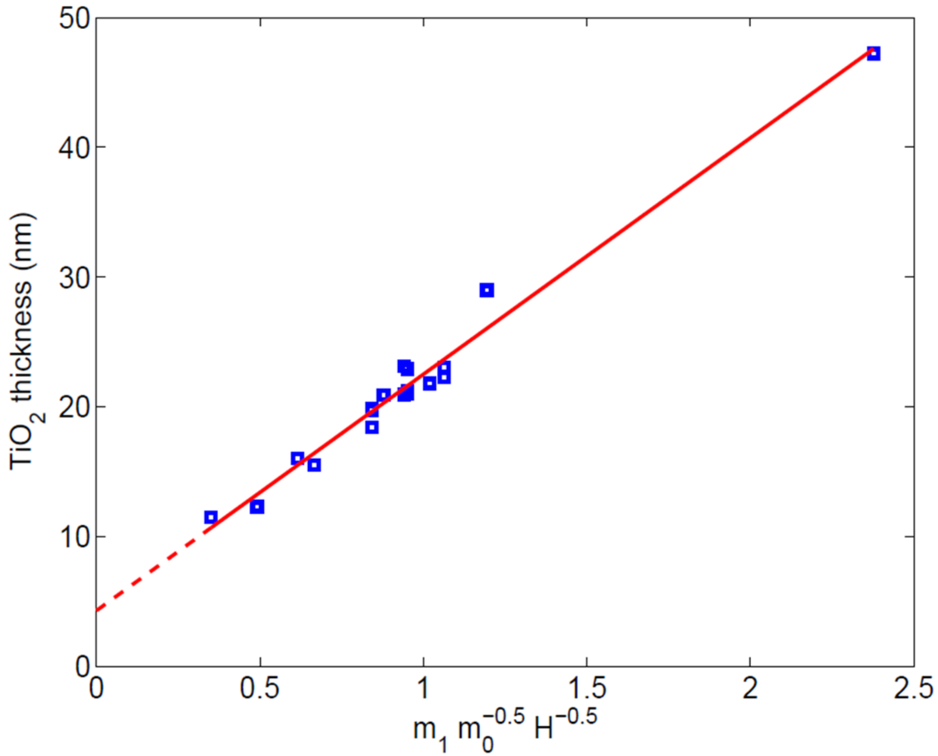
$$\frac{\dot{m}_1}{\dot{m}_0} \frac{e^{-E/kT}}{T} \frac{1}{\nu}$$

Thickness	$\dot{m}_0$	H	T
h_1	$\dot{m}_0$(1)	H(1)	T(1)
h_2	$\dot{m}_0$(2), $\dot{m}_0$(2')	H(2)	T(2)
h_3	$\dot{m}_0$(3)	H(3)	T(3)

TiO2 deposition from titanium isopropoxide

- **Online experiments**
  - Deposition is mass transport controlled
  - Knowledge of mechanism guides process efficiency improvements

$$\eta = \mathcal{F}(\dot{m}_0, \dot{m}_1, \dot{m}_2, H)$$



Questions

Materials and Design for Solar Applications

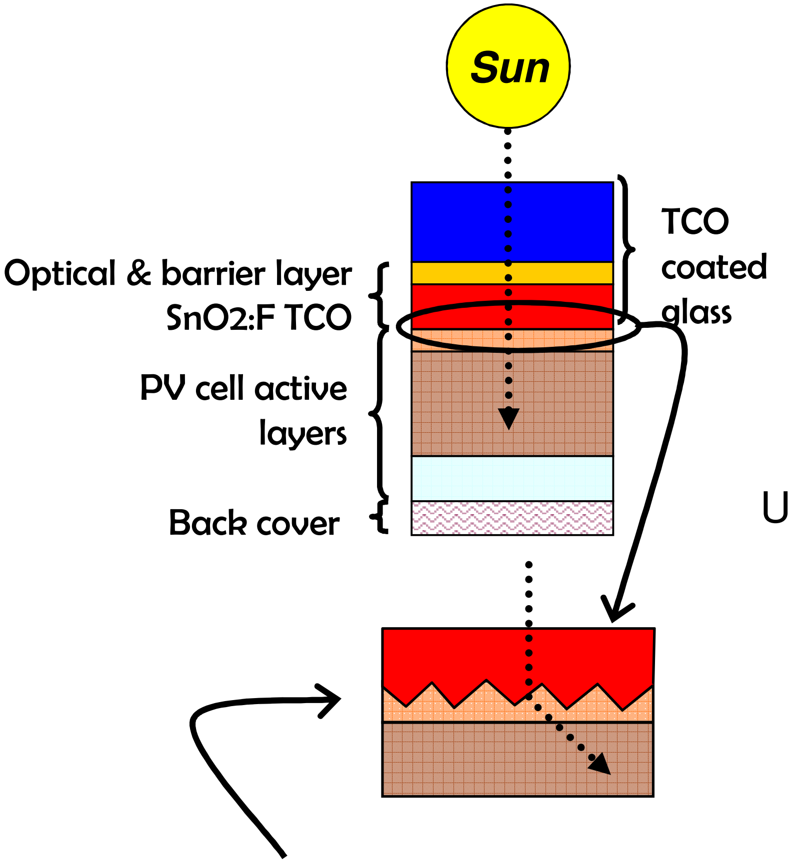
TCO → Transparent Conductive Oxide

Challenges for Solar Applications

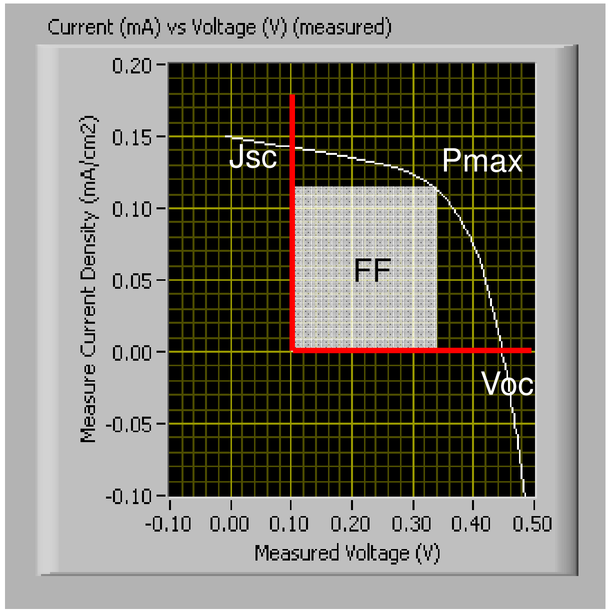
Drivers for Technology Development

- **Focus on $\$/W_p$ and Levelized Cost of Electricity**
- **Energy efficient manufacturing**
- **Device performance**
  - Optimize for device and application
- **Durable**
  - Long term optical performance
  - Mechanically durable

Glass and Coated Glass for Thin Film PV
Maximizing Performance is a Multi-factor Optimization



Understanding the device physics is critical



Interface morphology is critical to control light path through active layers

- *Rough typically used for thin film Si (above)*
- *Smooth needed for thin film CdTe*

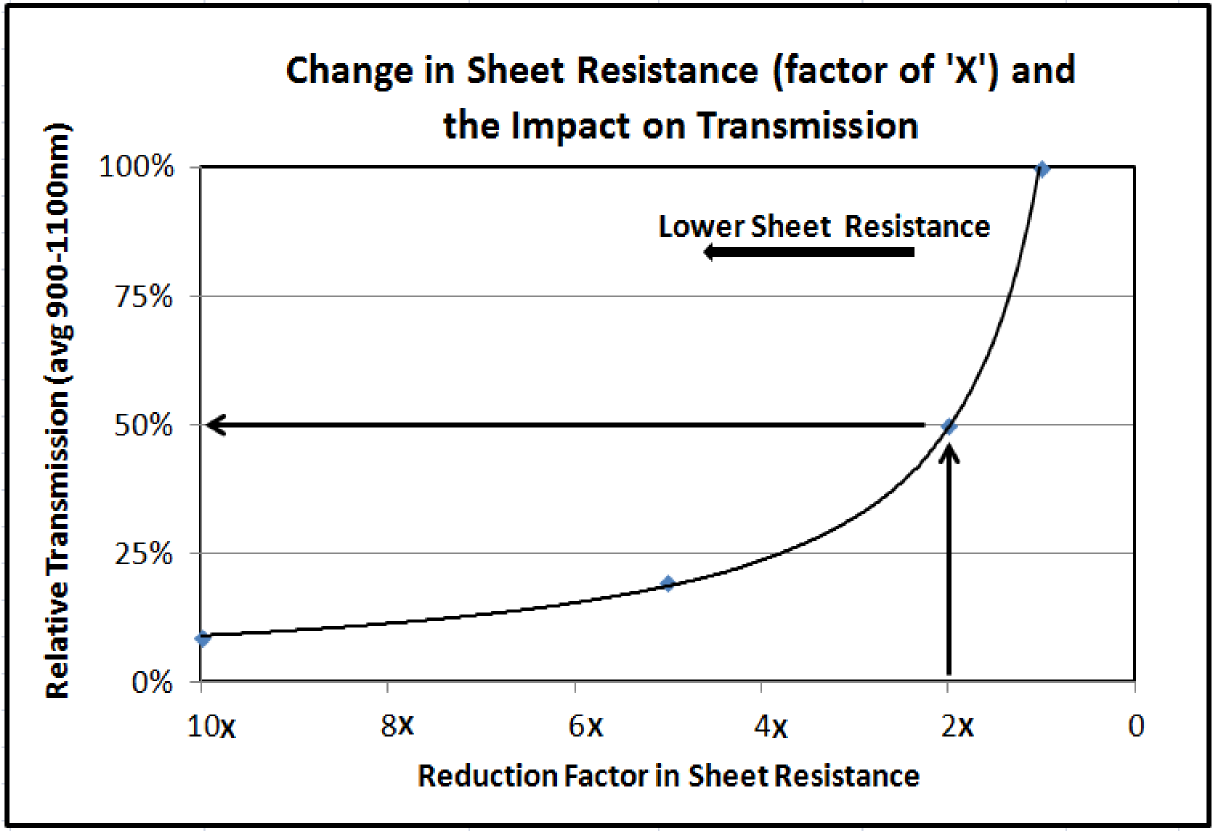
J_{sc}: Light management design

V_{oc}: TCO materials / interface

FF: TCO morphology

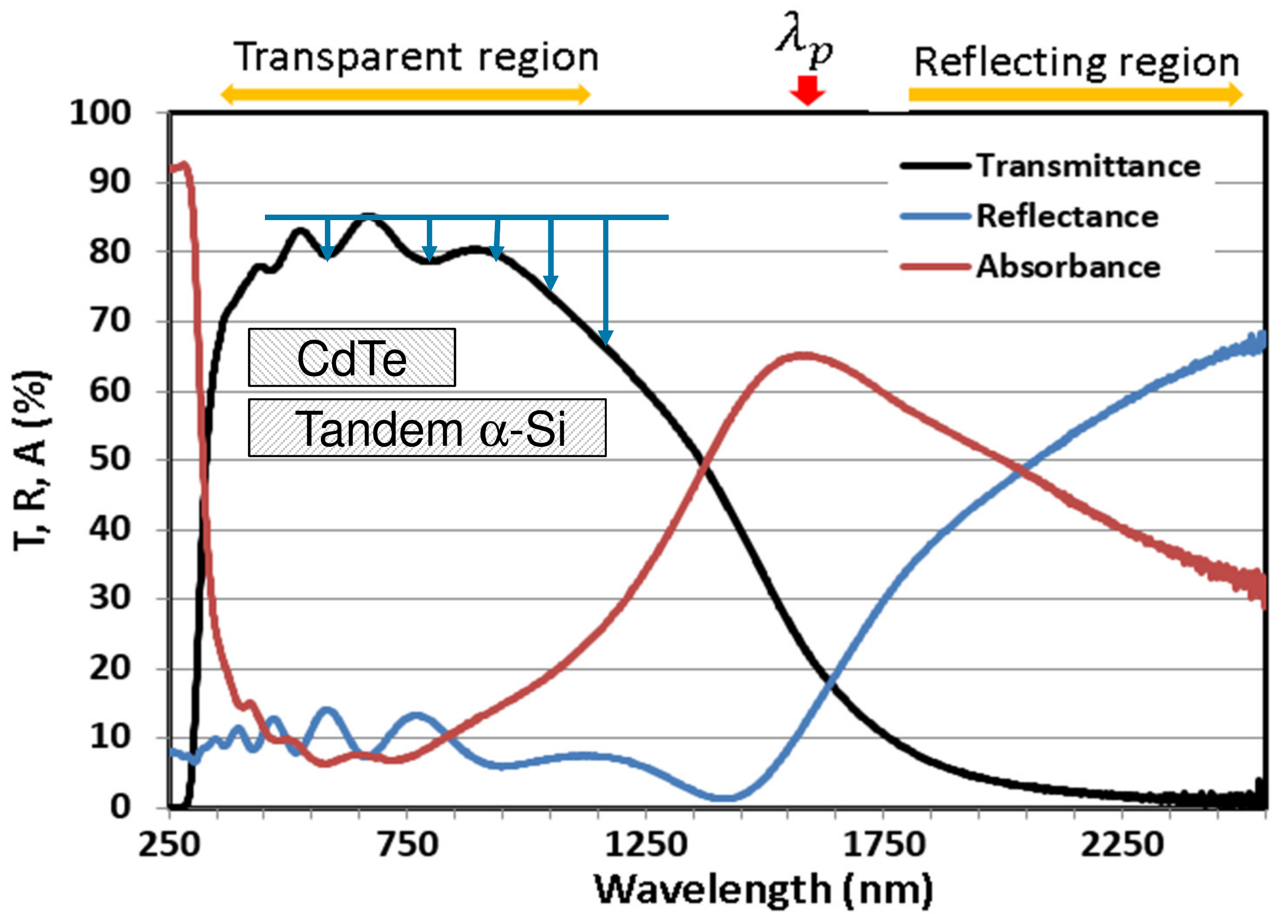
Design of High Performance Superstrates
TCO Coating Designs

In general electrical and optical properties of the TCO cannot be specified separately



Materials and Design

- **Impact of conductivity on PV performance**



$$\omega_p = 2\pi c/\lambda_p = \sqrt{\frac{ne^2}{\varepsilon_0 \varepsilon_\infty m_e^*}}$$

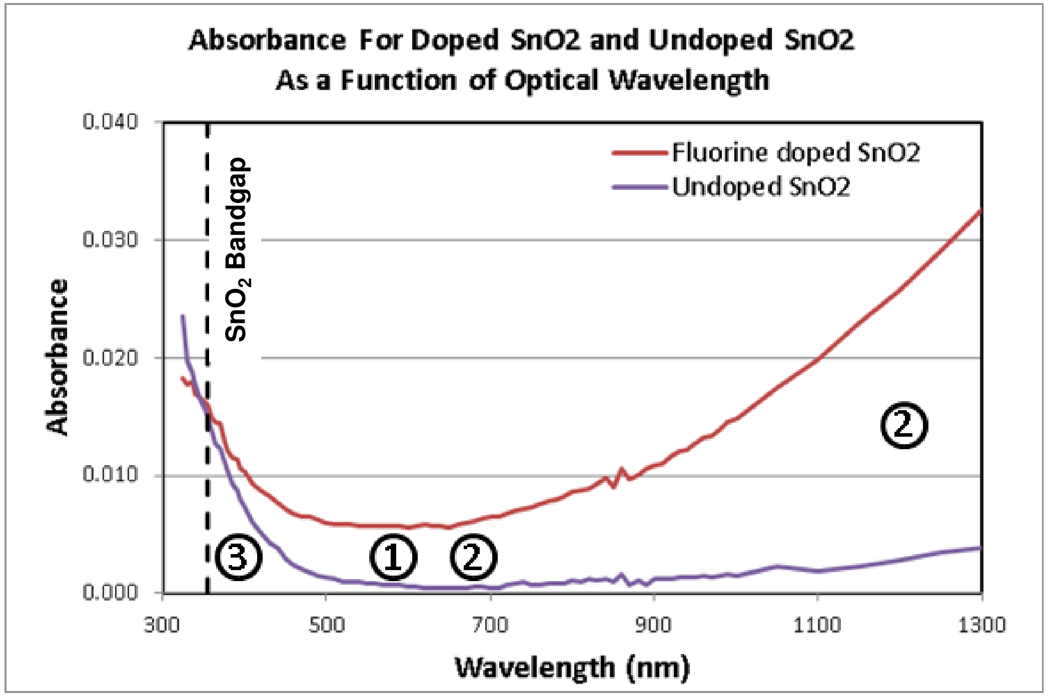
Engineering of the Bulk TCO to Reduce Optical Losses

- **Root causes of losses**
  1. Intrinsic absorption
  2. Free carriers

$$\lambda_p = \frac{2\pi c}{\omega_p} = 2\pi c\sqrt{\frac{\varepsilon_o \varepsilon_\infty m^*}{ne^2}}$$

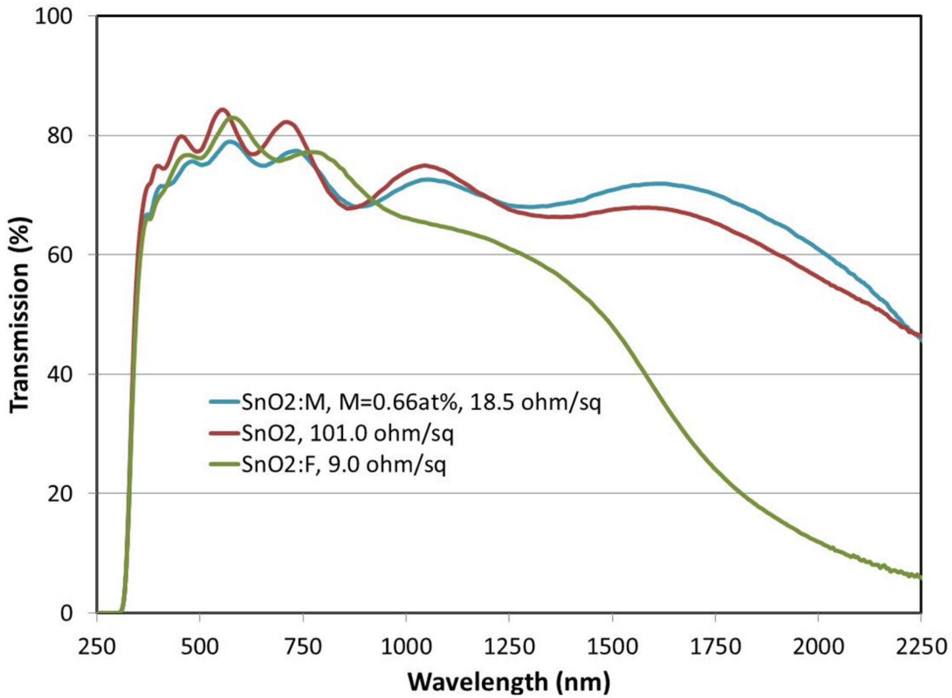
  3. Bandgap

- **Materials engineering and design**
  - Film quality
  - Increase Permittivity
  - Increase Mobility
  - Increase Bandgap



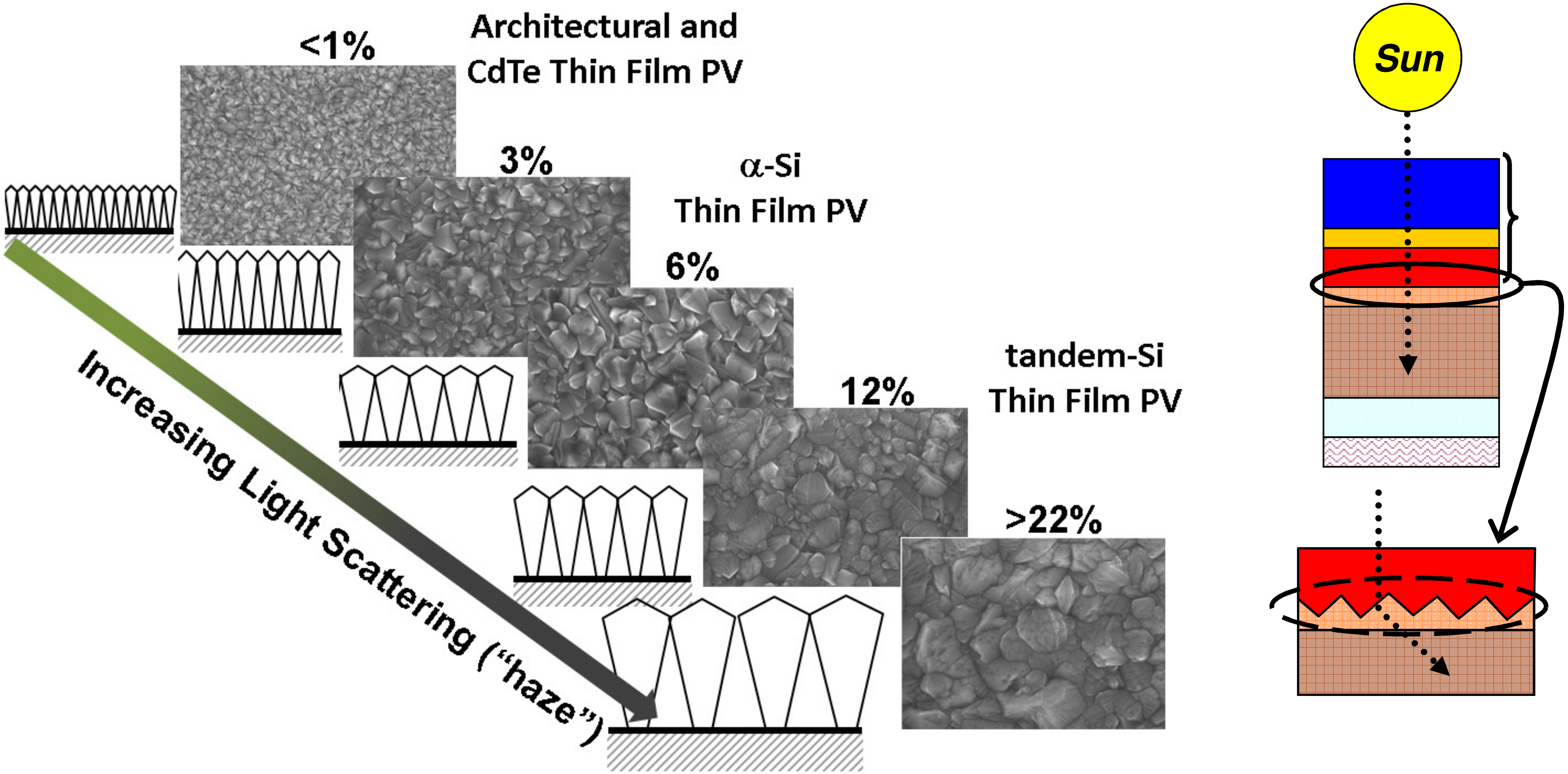
Materials Engineering – reducing optical losses

- Alloying of SnO_2 matrix to modify permittivity
- Electrical properties comparable to SnO_2:F
- Optical properties comparable to undoped material



Light Redirection by Morphology Engineering

- **Increased optical path length through PV active layer**



Morphology Design – Tandem α-Si PV

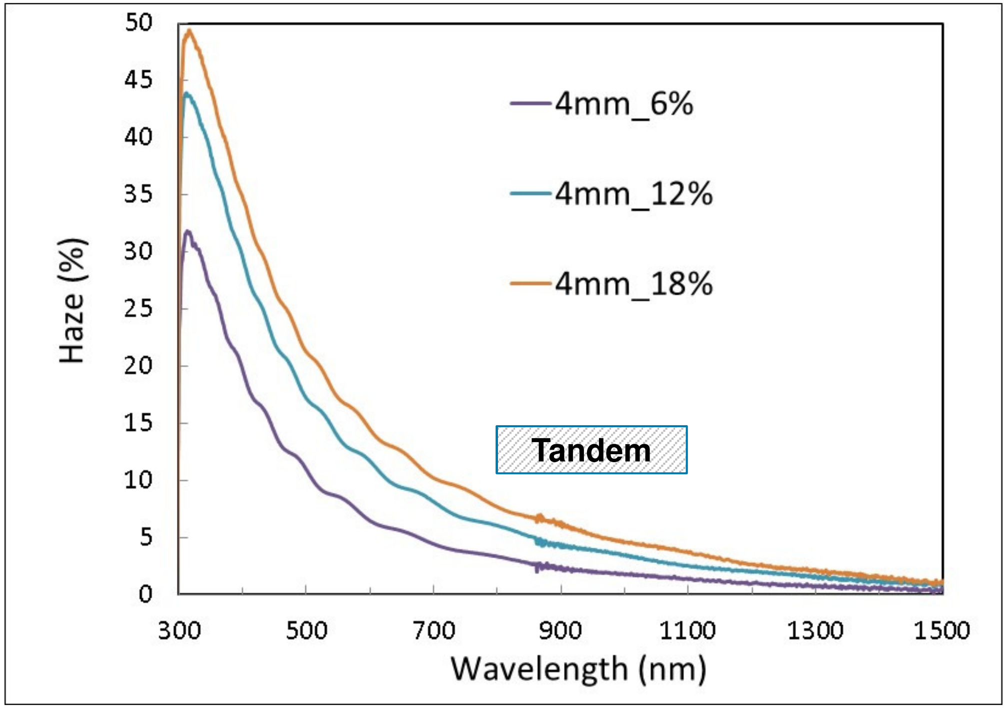
- **What is optimal crystal size for maximizing scattering in region of interest?**
  - Small sized

    Mie scattering
  - SnO_2/Si interface

    Optical indices
  - Ensemble of sizes

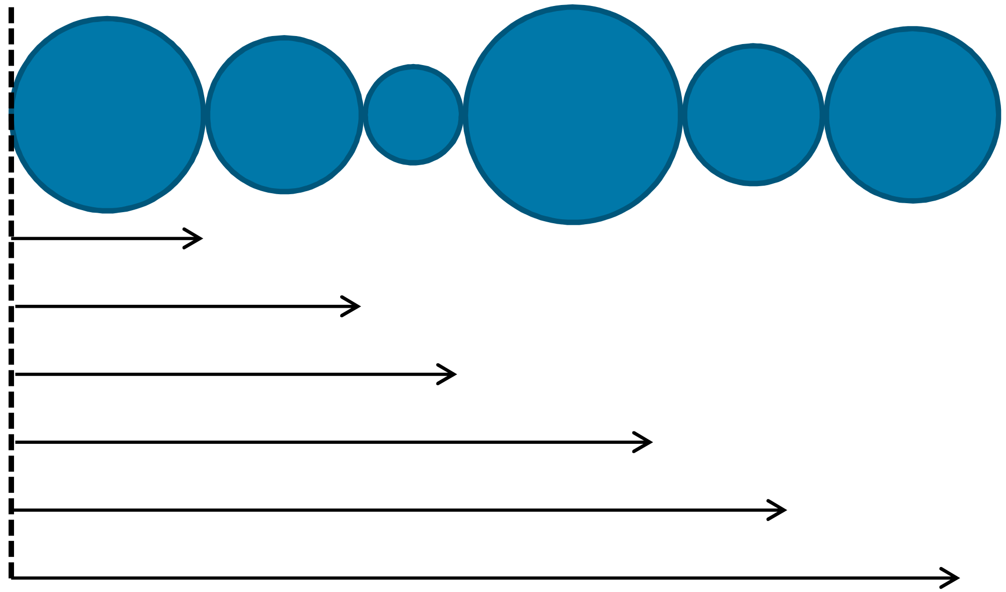
    form of distribution statistics

Light Scattering Spectra (2º cone)



Morphology Design
Determination of form of Distribution

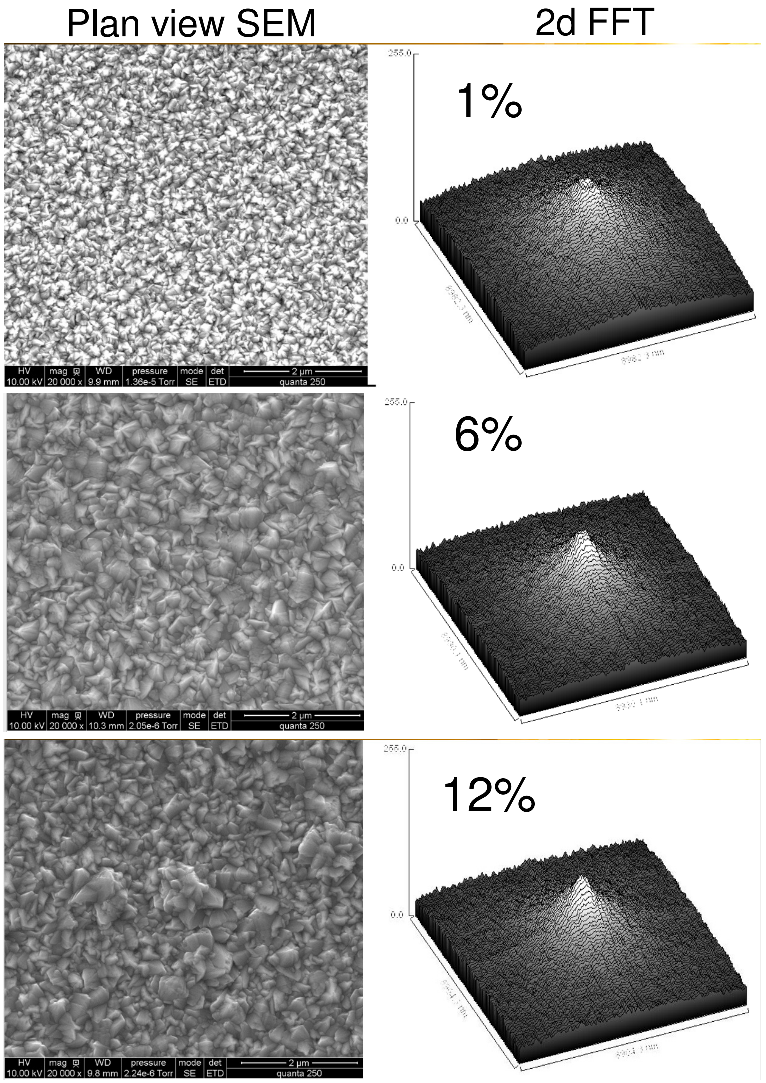
- Consider an ensemble of grains with distribution $\mathcal{G}$
- Determination of form is difficult in $\mathcal{R}$ space – map into Fourier space

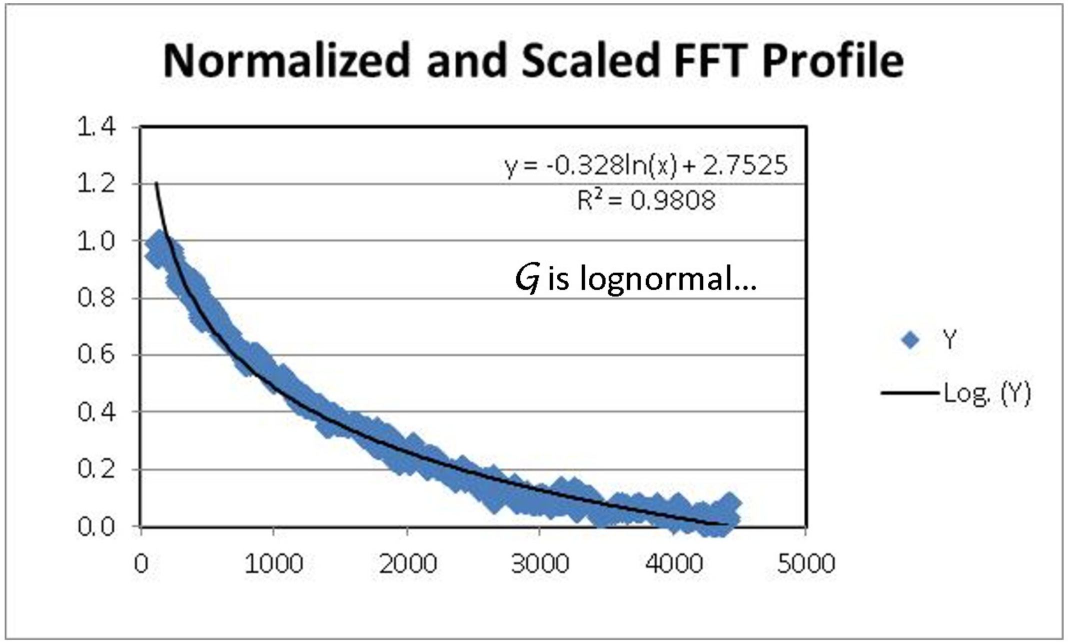


Normal Distribution $\frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$ $k \propto \frac{1}{x}$

Lognormal Distribution $\frac{1}{x\sqrt{2\pi\sigma^2}} e^{-\frac{(\ln x-\mu)^2}{2\sigma^2}}$ $k \propto \frac{1}{\ln(x)}$

Grain Size Distribution Scales and is Lognormal



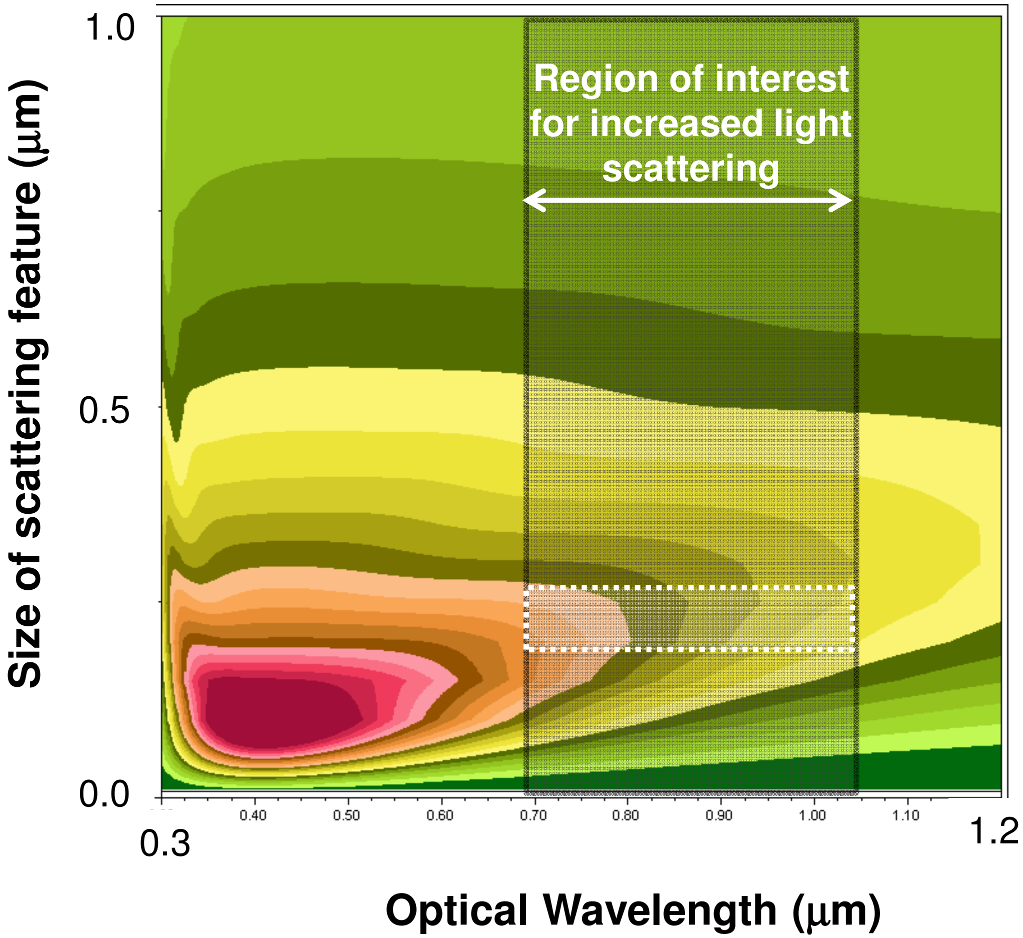


Optimization of Grain Size / Morphology

Scattering amplitude vs. wavelength for different sizes of scattering features (SnO_2/Si interface)

- **Distribution of sizes (lognormal, σ=20% of μ)**
- **For structures in Si, calculations indicate long length scale features should be ~0.2μm**

Red is high scattering
Dark green is low scattering

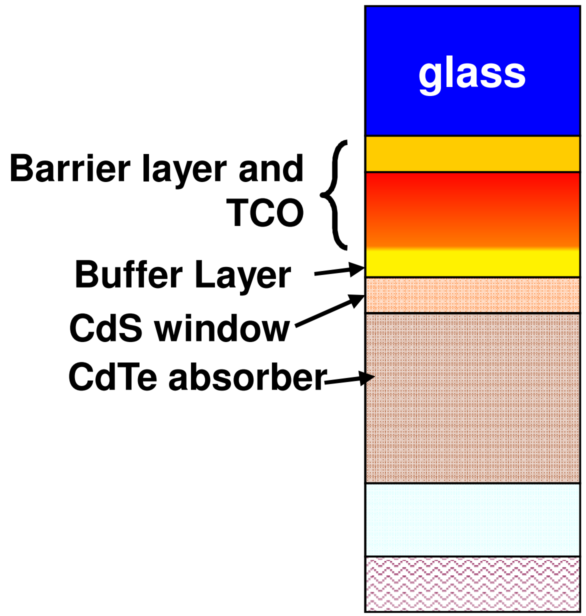


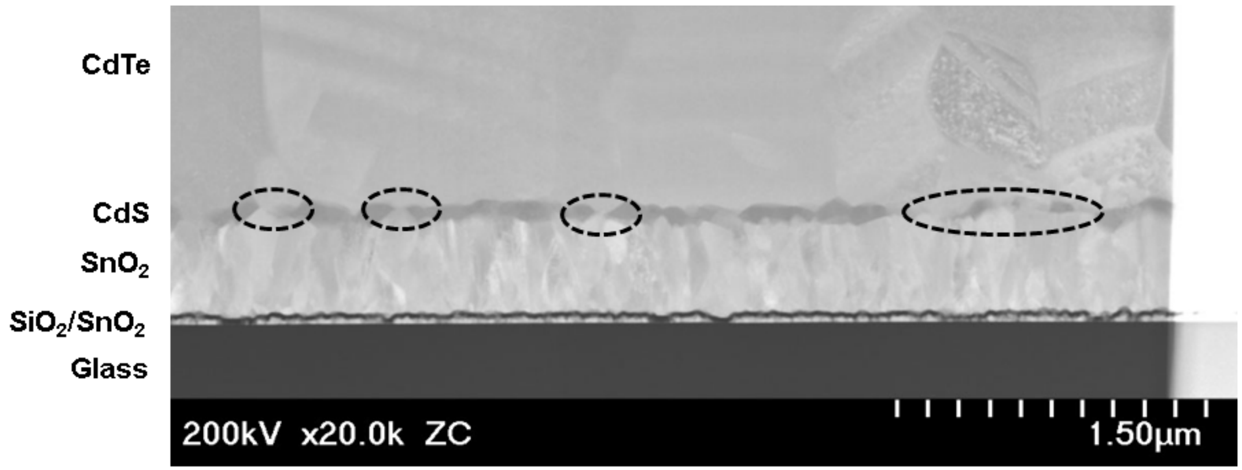
Interface Design – CdTe

- **Role of the buffer layer**

Buffer layers

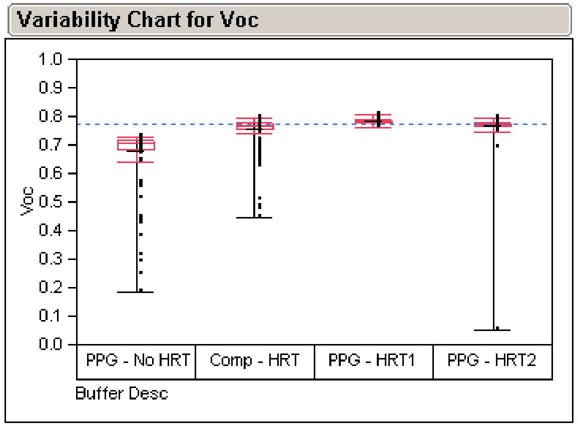
- Typically *i*-SnO_2 or in the ZnO-SnO_2 system
- Very high resistance (1000+ Ω-cm)

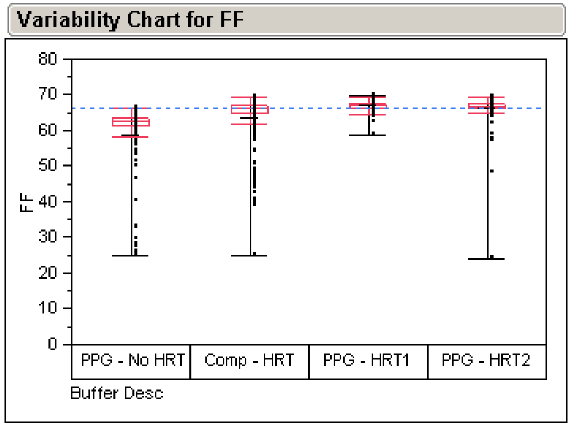


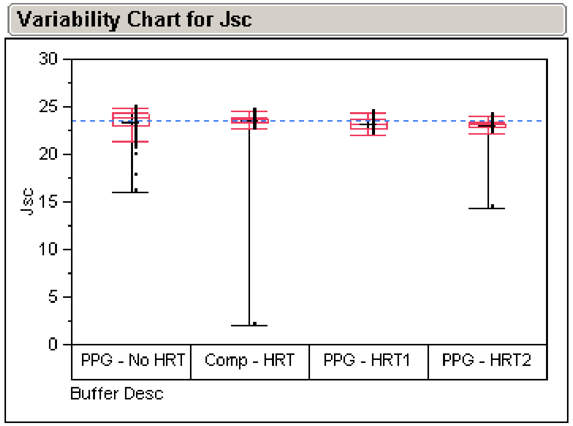


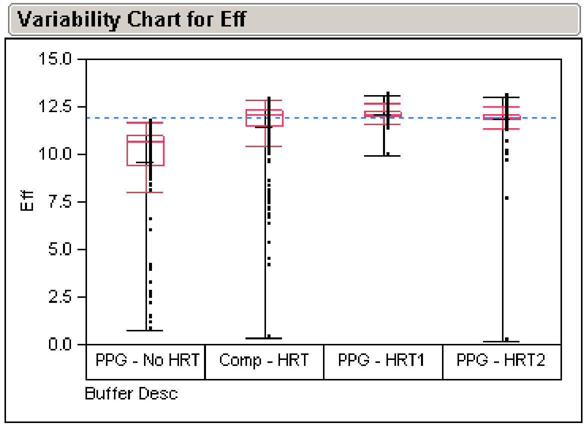
Device Performance with Buffer Layer

- **Device structure**
  - 50 nm CdS
  - 850 nm CdTe
- **Process**
  - Magnetron sputtering
  - Low substrate temp
- **Results**
  - HRT1
    increased efficiency
    increased process robustness









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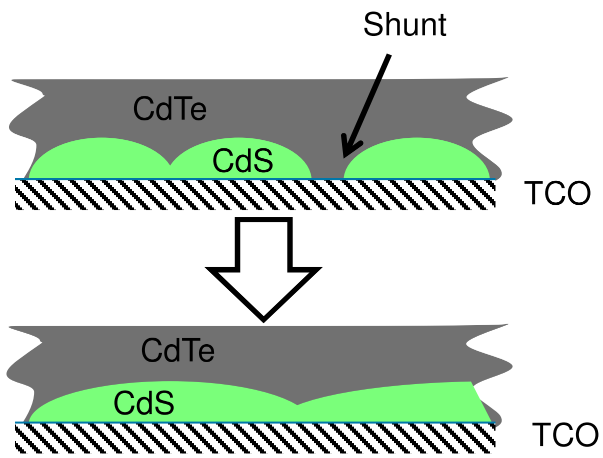
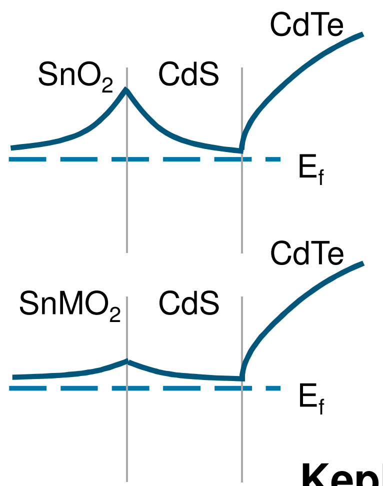
Function of the Buffer Layer – Two Hypothesis

- **Buffer layer reduces the number of shunts**
  - Surface energy of the buffer material changes the CdS growth mode
  - CdS morphology has fewer pinholes for shunts



- **Buffer layer modifies the band alignment**
  - Material's properties and / or interface states create barriers
  - Barriers reduce Voc of device



Kephart, et al., IEEE 39th PVSC

Summary

- **CVD is effective technique for large area high volume production of low-E coatings that reduce transport of thermal radiation**
  - Control of emissivity
  - Color and aesthetics
- **CVD can produce TCO coatings for thin film PV applications**
  - Engineering of interface roughness and band alignment
  - Materials and stack design for control of electrical and optical properties
- **Process and equipment design**
  - Robust process and equipment
  - Design of process through basic materials properties
  - Mass transport or reaction control of deposition

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