# A Colloidal Nanoparticle Form of Indium Tin Oxide

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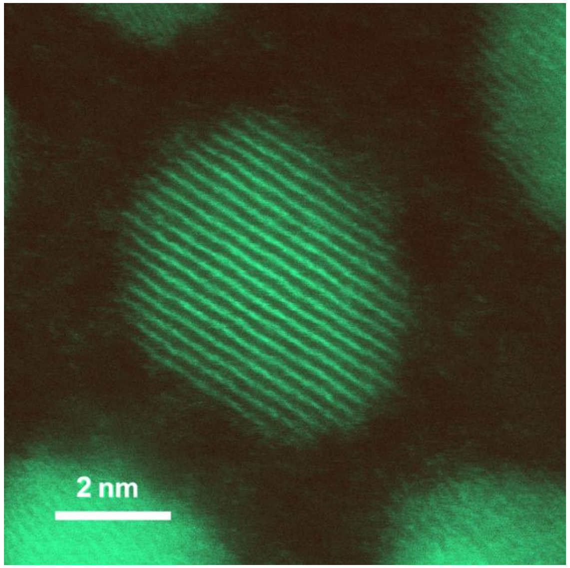
# Overview

- Introduction & Motivation
- Background
  - Basic Physics of ITO
- System Synthesis
- Basic Material Properties
- System Optimization
- Electron Generation
- Summary



# Introduction & Motivation

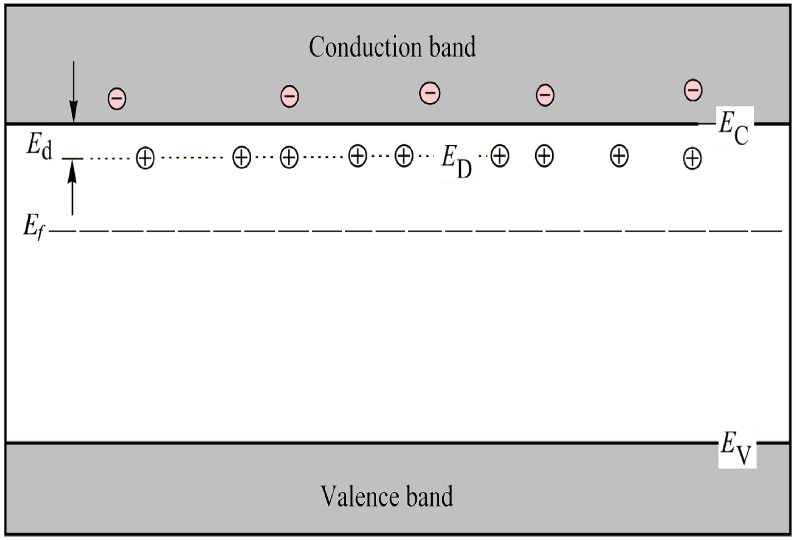
- Indium Tin Oxide (ITO):
  - Most widely used Transparent Conductive Oxide (TCO) material.
  - Essential material for all LCD and Plasma displays….currently.
  - Additionally: Anti-static, heat dissipation, organic LEDs, CIGS solar
  - Demand/Supply ratio rising dramatically.

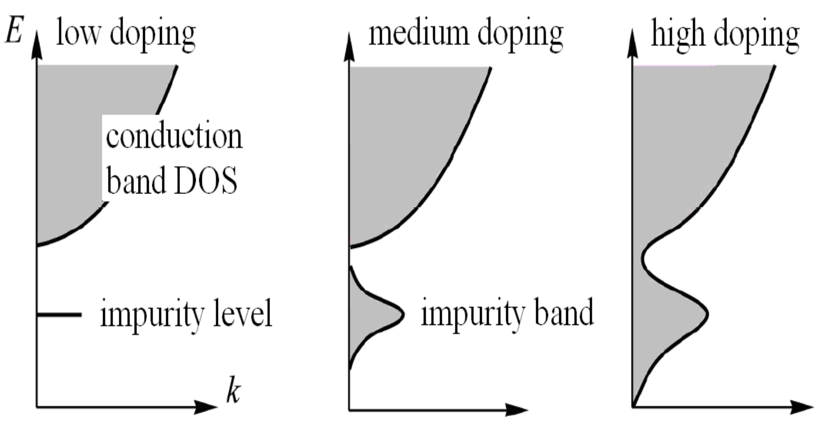
- Interest in a solution-dispersible nanoparticle form:
  - Inkjet Printing of TCOs – process speed and less Indium waste.
  - Dip-Coating for more complex geometries.
  - Ideal system is composed of crystalline nanoparticles that can be homogeneously dispersed in an ink solution with no agglomeration.

- A methodology has been developed to produce a colloidal nanoparticle form of ITO that specifically meets these requirements.

- Functional properties can be optimized prior to application.
- Allows study of ITO by new methods.
- Process can be scaled for mass-production.

# Background: Transparent Conductivity



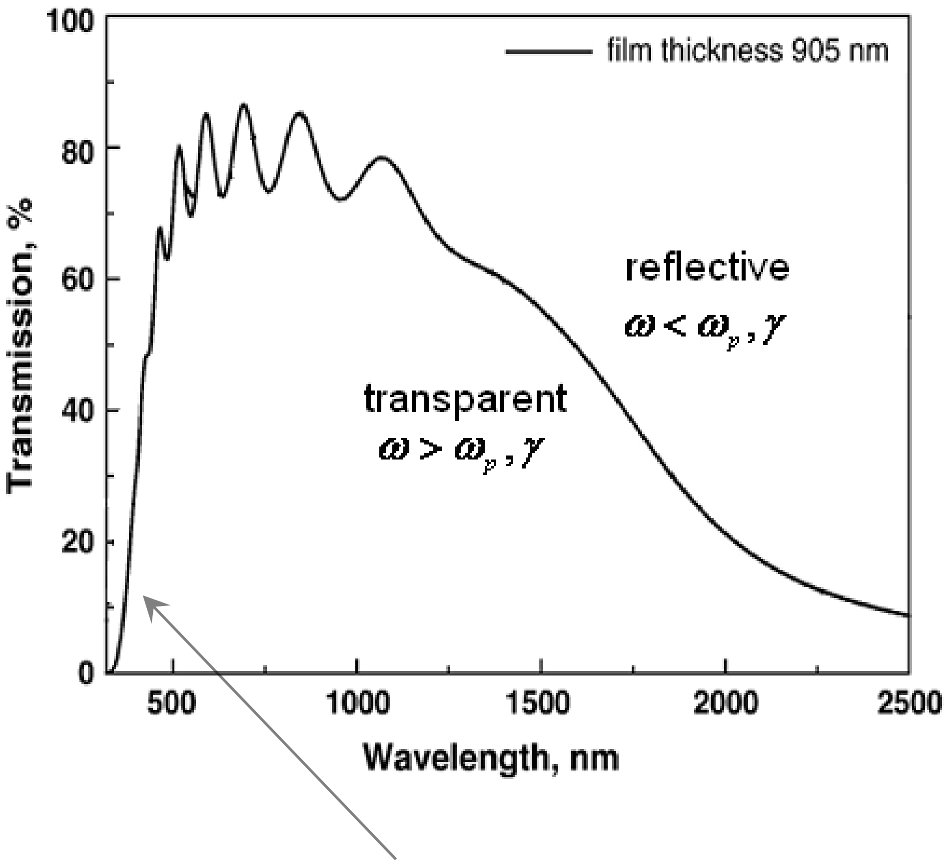

- Degenerate doping of wide band gap >3eV
  - dopant of higher valence for n-type.
  - Impurity potentials w/ activation energy $E_D$
  - Spatial extent is electron Bohr radius,

$$a^* = \left(\frac{\varepsilon_\infty}{m_c^*}\right)\left(\frac{\hbar^2}{\pi e^2}\right) \cong 1.35nm\_(ITO)$$

- Increased doping promotes wavefunction overlap
  - Low: impurity levels are discrete w/o significant interaction.
  - Medium: potentials interact, split, and form an impurity band.
  - High: wavefunction overlap to allow conduction by at low temperature.
- Mott Criteria: Semiconductor-to-Metal Transition
  - assuming a Poisson distribution of impurities,

$$2a_B^* = \frac{3}{2\pi} N_{crit}^{-1/3} \qquad N_{c\cong} 5.62x10^{18} cm^{-3}\_(ITO)$$

# Background: Optical Properties of ITO




Band Gap Expansion due to Conduction Band Filling

- "Optical Window" between UV and IR regions.
  - Lorentz oscillator model and Drude theory for the free-electron plasma.

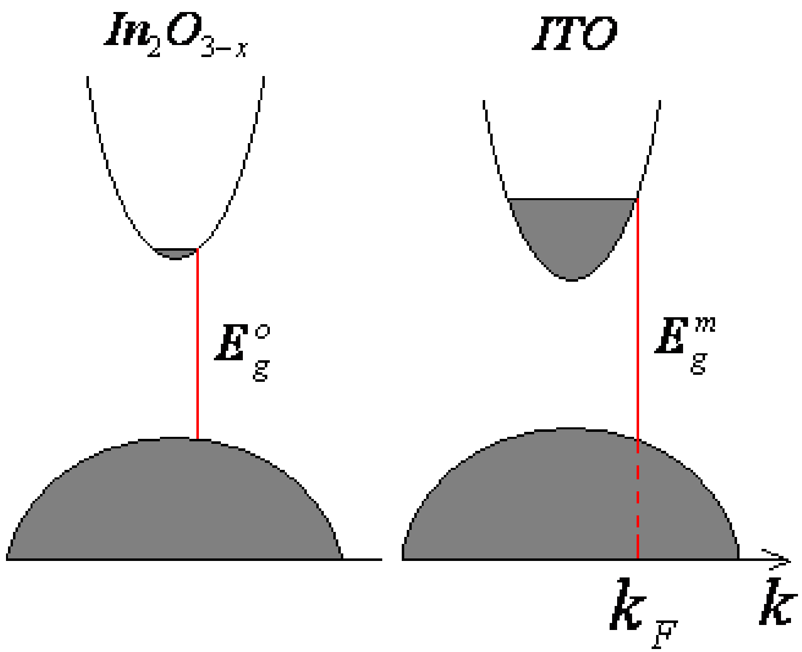
$$\varepsilon(\omega) = (N - iK)^2 = \varepsilon_\infty \left[ 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} - i \frac{\omega_p^2 (\gamma / \omega)}{\omega^2 + \gamma^2} \right]$$

  - Plasma Frequency

$$\omega_p = (ne^2 / \varepsilon_0 \varepsilon_\infty m_c^*)^{1/2}$$

  - Dielectric behavior for $\omega > \omega_p , \gamma$
  - Reflective behavior for $\omega < \omega_p , \gamma$

# Background: Conduction Band Filling




- Undoped Indium Oxide is slightly degenerate due to low level of oxygen vacancies.
- Donor doping with Sn promotes CB filling and band gap expansion … Burstein-Moss effect.

$$\Delta E_g^{BM} = \frac{\hbar^2}{2m_{vc}^*} k_F^2 \qquad k_F = (3\pi^2 n)^{1/3}$$

(effective masses determine fill rate)

- Above the Mott criteria, Many-Body Interactions promote Band Gap Narrowing.

(Coulomb interactions, mutual exchange forces, and attractive impurity scattering)

$$\Delta E_g^{BGN} = \frac{e^2 k_F}{2\varepsilon_\infty \pi^2}$$

(exchange interactions only)

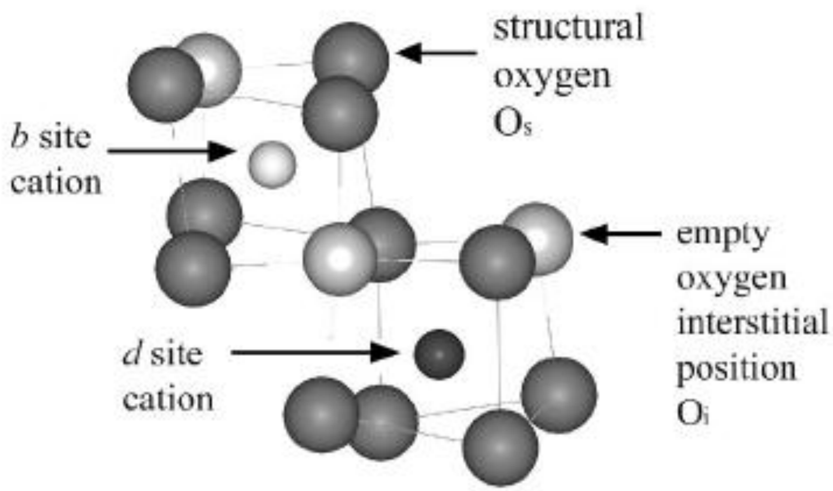
Total Band Gap Expansion

$$E_g^m - E_g^o = \Delta E_g^m = \Delta E_g^{BM} - \Delta E_g^{BGN}$$

$$\Delta E_g^m = \frac{\hbar^2}{2m_{vc}^*}(3\pi^2 n)^{2/3} - \frac{e^2}{2\varepsilon_\infty \pi^2}(3\pi^2 n)^{1/3}$$

# Background: Frank and Kostlin Defect Model

Indium Oxide - Bixbyite



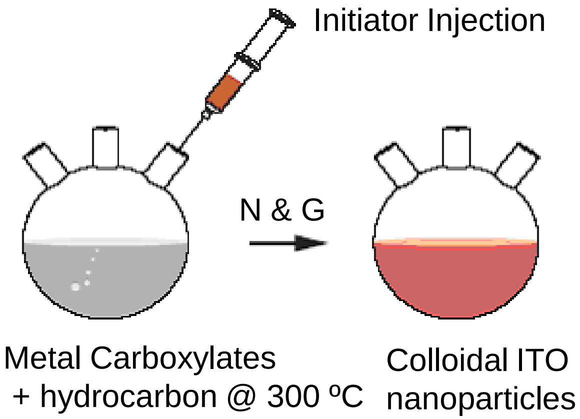

- Prevalence of these clusters will increase with Sn content.

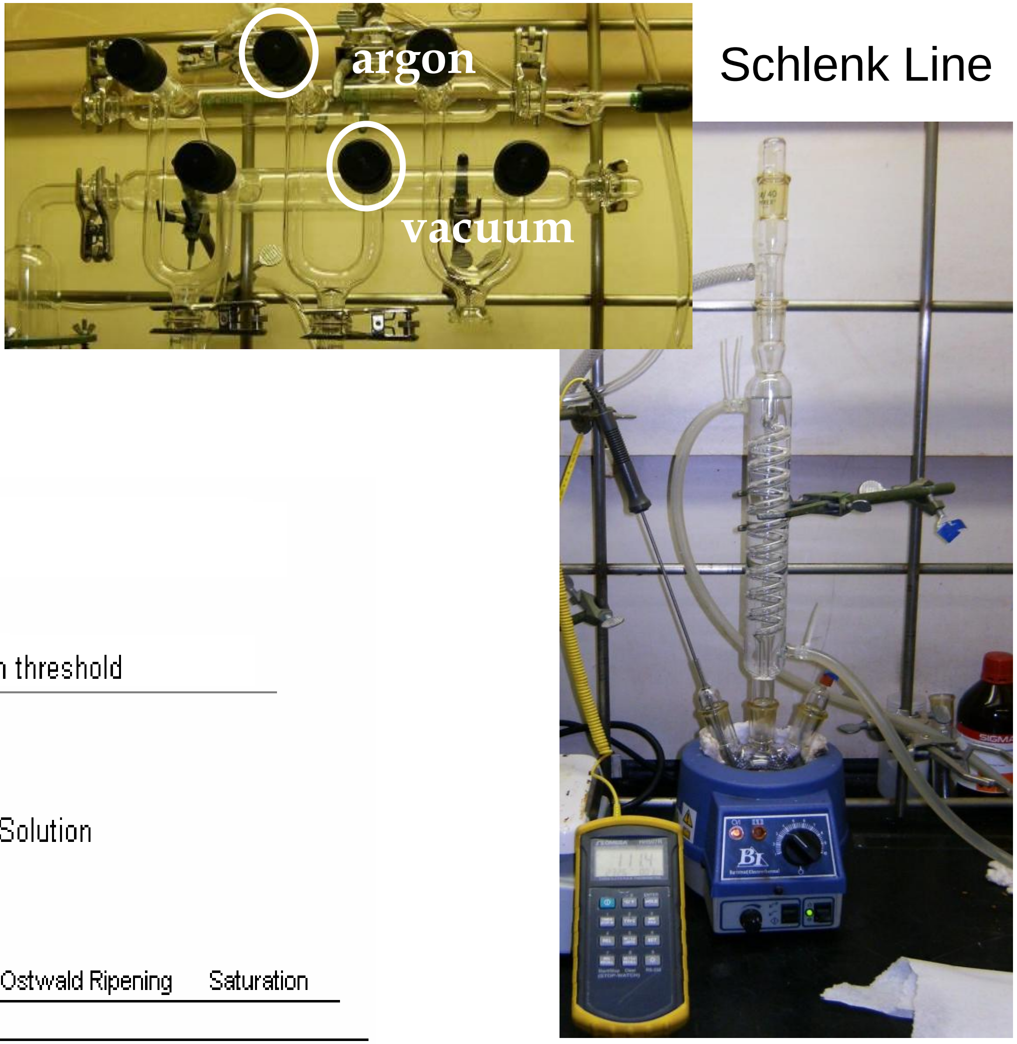
- Sn(4+) substituting In(3+) = Sn*
- $(2Sn_{In}^{\bullet}O_i^{''})^x$ neutral associates
  Frank and Kostlin (1982)
- Reduction yields ***n*** per:

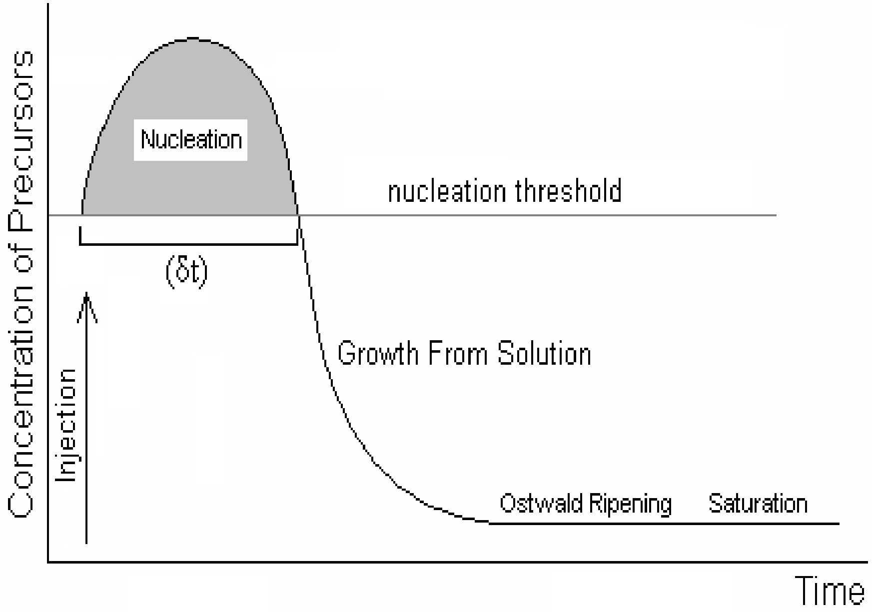
$$(2Sn_{In}^{\bullet}O_i^{''})^x \rightarrow \frac{1}{2}O_2(g) + 2Sn_{In}^{\bullet} + 2e'$$

- $O_i''$ absent in $In_2O_3$ and always present in ITO.
- Ratio of Sn to $O_i''$ in oxidized ITO ~2
- Nearest-neighbor Sn-$O_i$-Sn associate clusters "trap" interstitial oxygen.

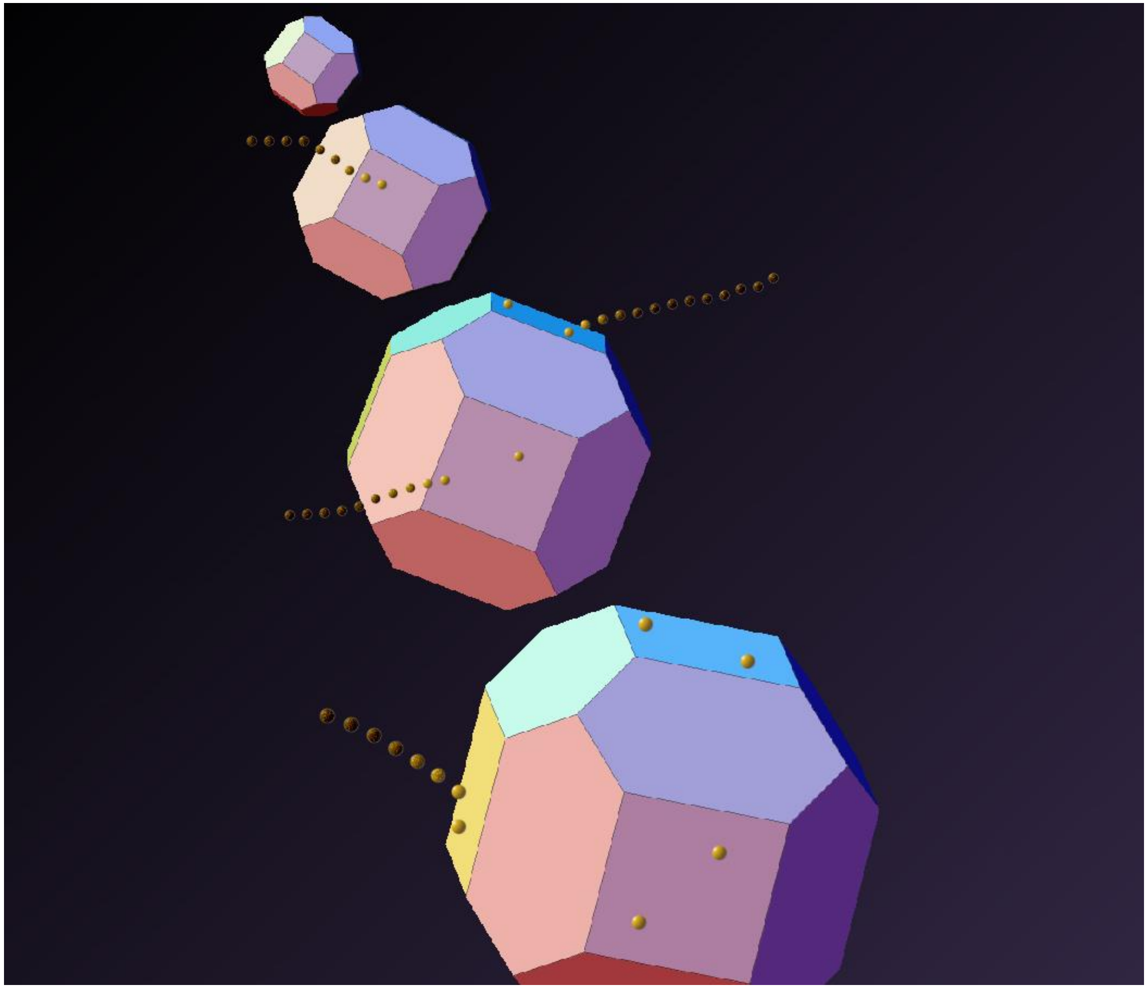
# System Synthesis : Rapid-Injection Method



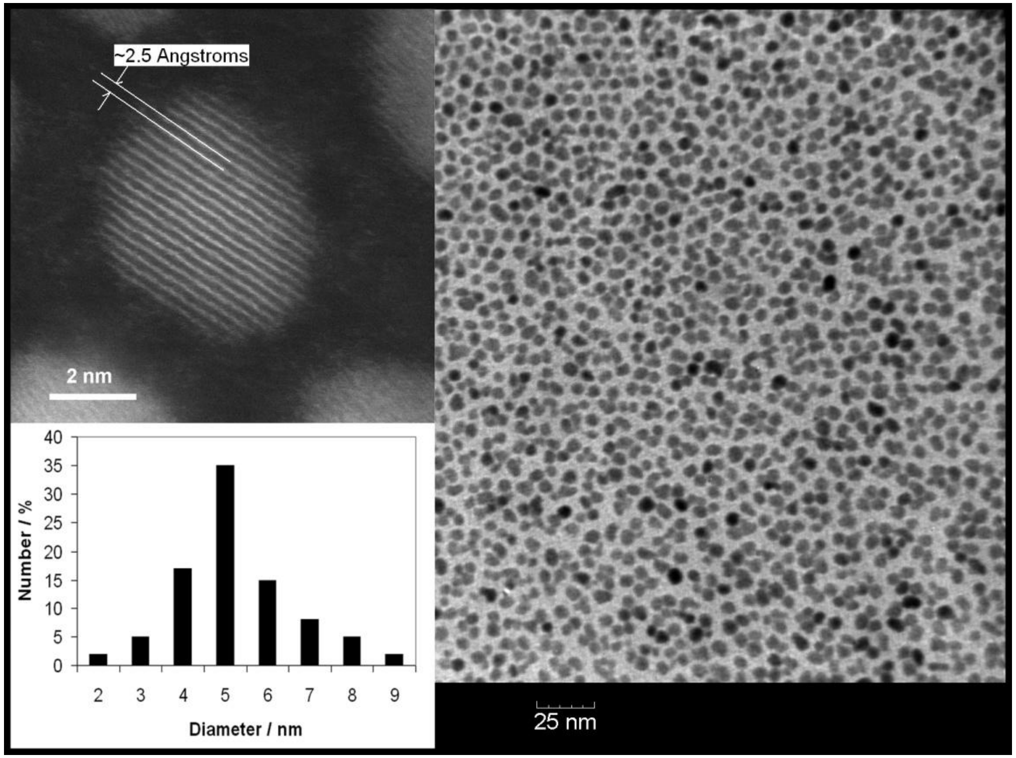



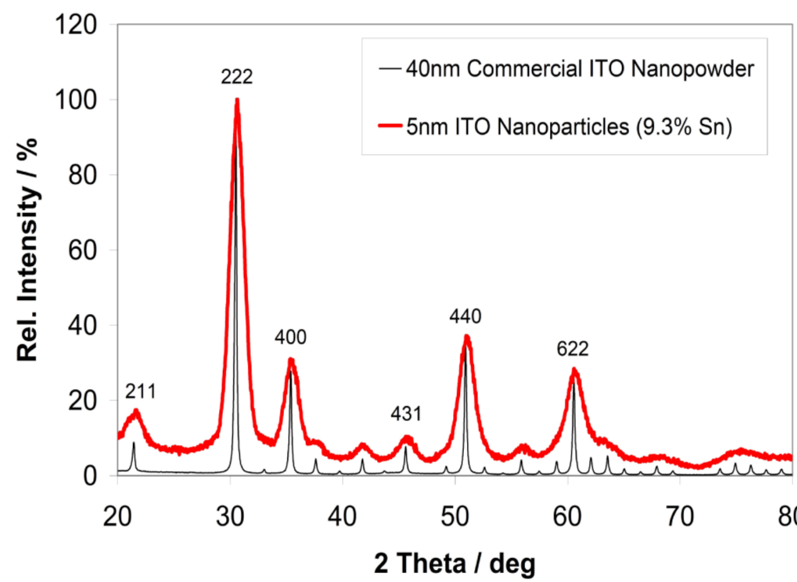
# Diffusive Growth From Solution



# Basic Properties: Composition, Phase, Morphology



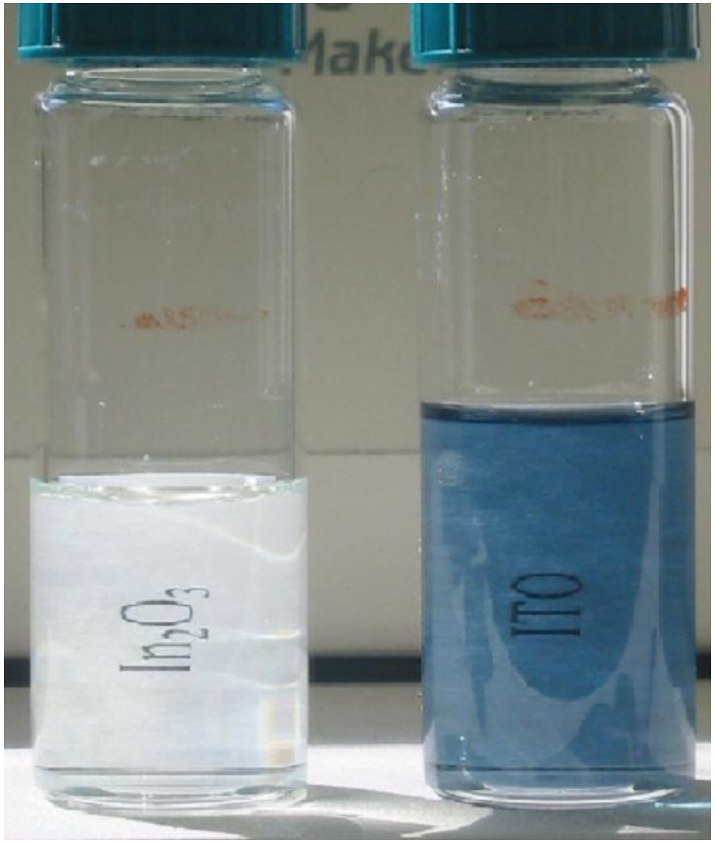

- Injection of primary amine at 300C
- Octadecylamine
- Highly crystalline particles
- ~5.4nm with narrow size distribution
- 9.3% Sn measured by ICP-MS
- No tin oxide phases observed.




400 planes observed in the inset.

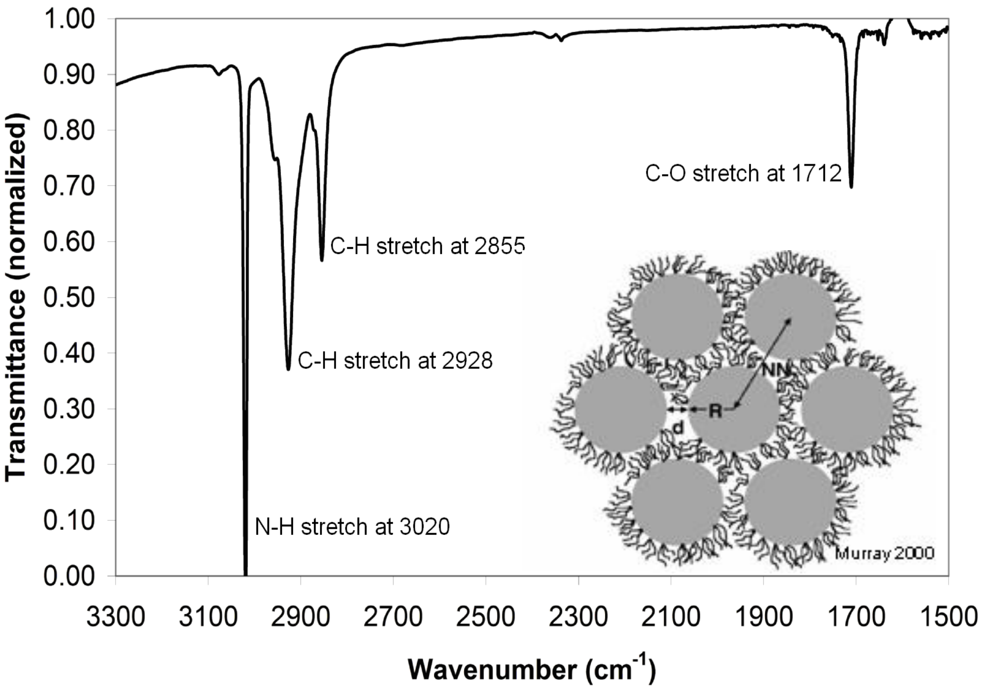
# Basic Properties: Surface Ligand Characteristics

Colloidal Nanoparticles, dispersed in hexane.

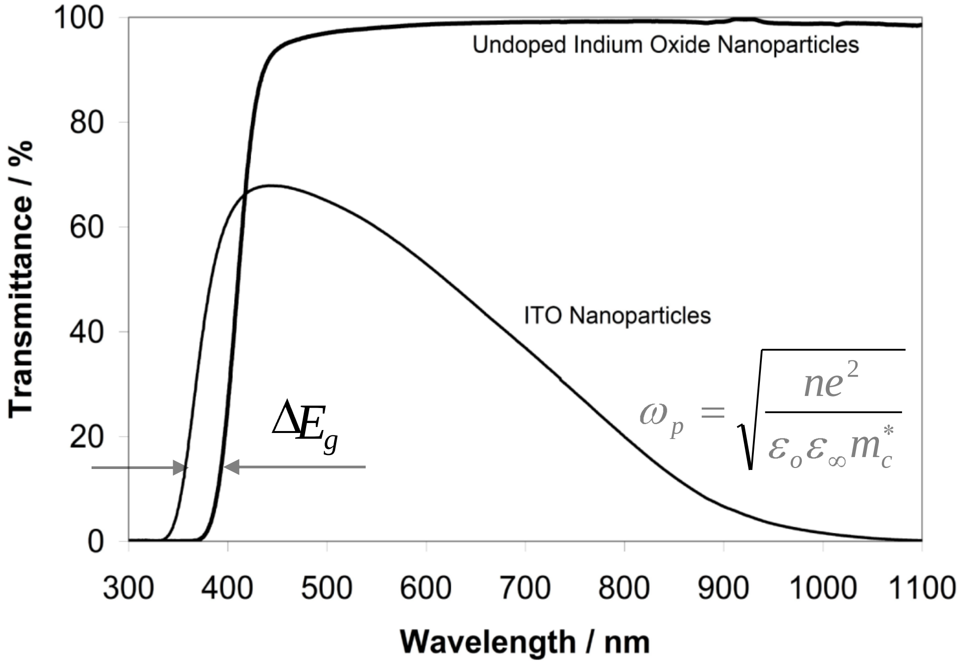


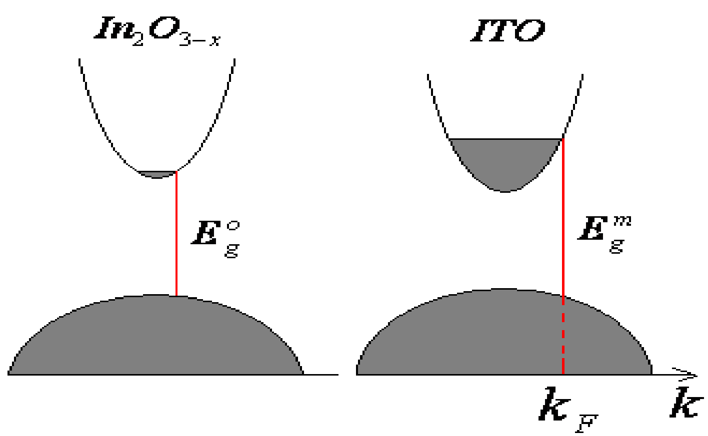

Indium Oxide Indium Tin Oxide

- Dispersible with no agglomeration (months / years at room temp.)
- FT-IR analysis of purified and re-dispersed solution.
- C-H and C-O stretch of carboxylic acid. N-H stretch of amine.

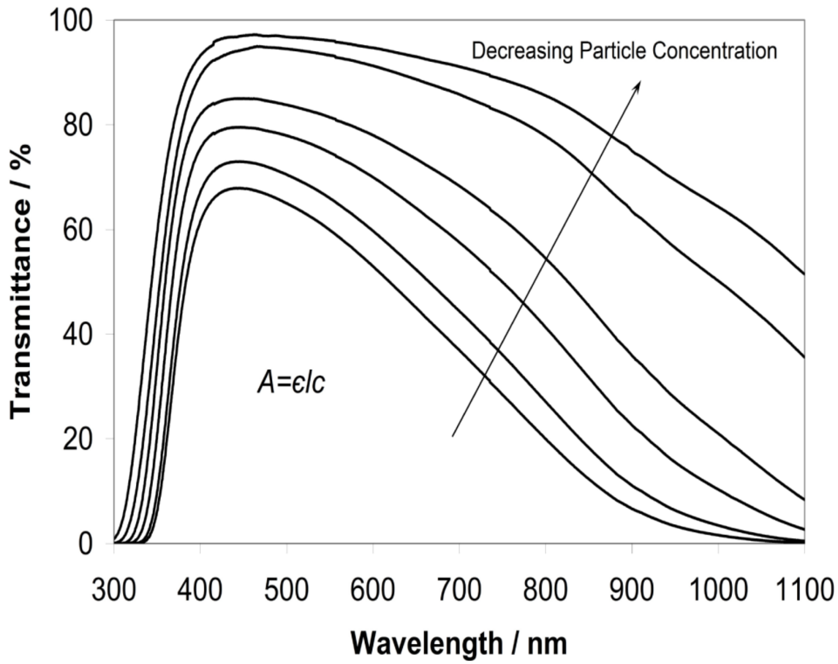


# Basic Properties: Optical Properties (Indium Oxide vs ITO)



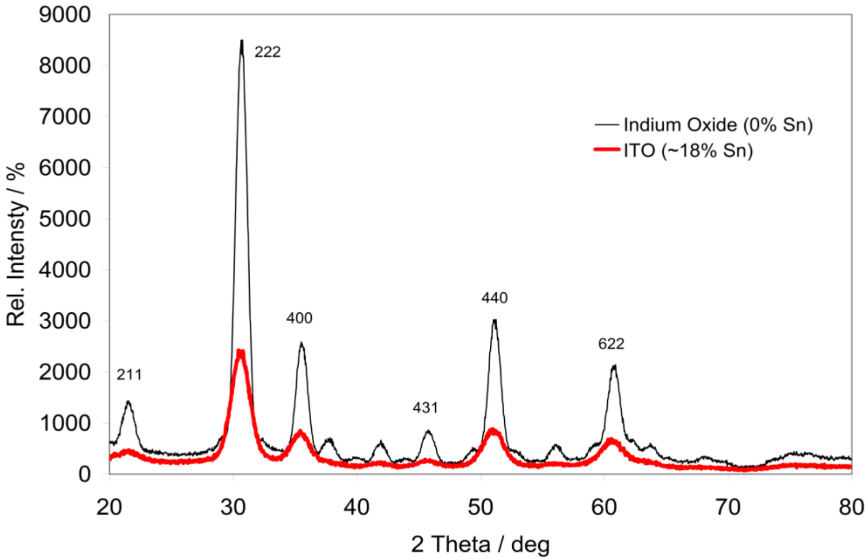



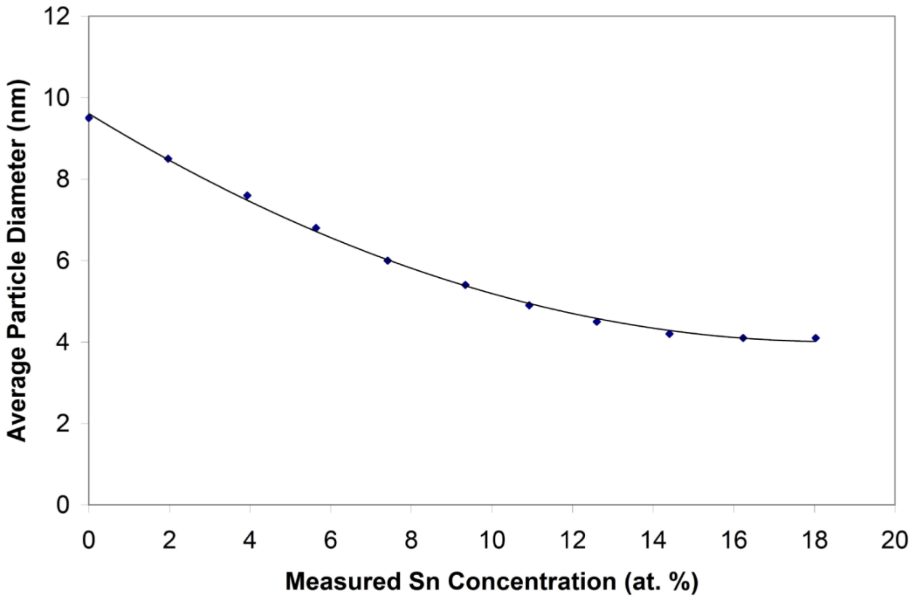

- Concentrated colloidal dispersions in hexane.
- Clear reflection edge and $\Delta E_g^m$ observed in ITO.
- Dilution effect (Beer-Lambert).

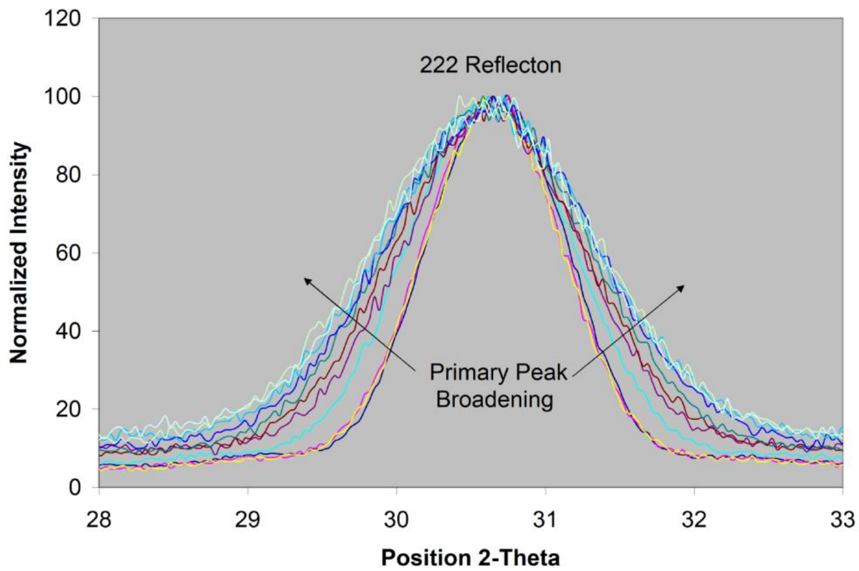


# System Optimization: Dopant Concentration Studies

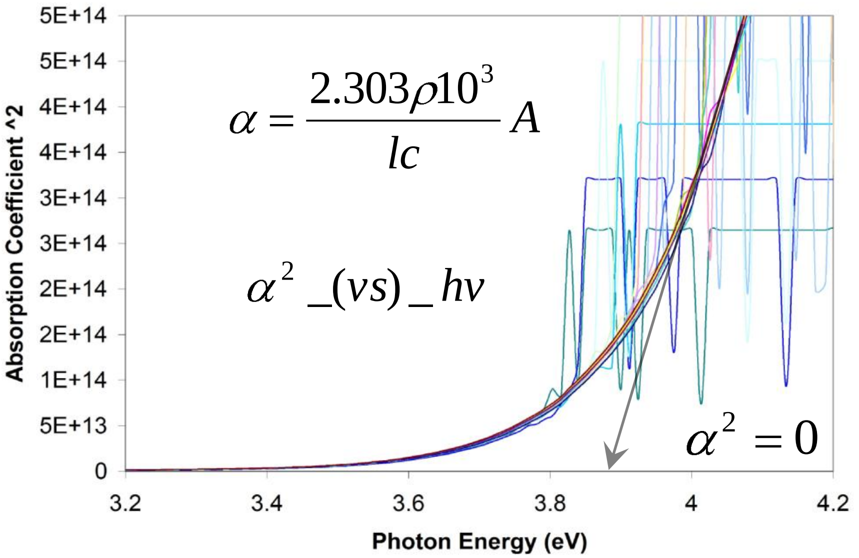
| Sn (%) Used | Sn (%) ICP | Doping Eff. (%) | Phase ID | SnO or $SnO_2$ | Particle Diamter (nm) | Lattice Parameter (Å) |
|---|---|---|---|---|---|---|
| 0 | 0 | n/a | $In_2O_3$ | none | 9.5 | 10.1225 |
| 2 | 1.97 | 98.51 | $In_2O_3$ | none | 8.5 | 10.1282 |
| 4 | 3.93 | 98.36 | $In_2O_3$ | none | 7.6 | 10.1301 |
| 6 | 5.64 | 93.97 | $In_2O_3$ | none | 6.8 | 10.1327 |
| 8 | 7.42 | 92.70 | $In_2O_3$ | none | 6 | 10.1351 |
| 10 | 9.34 | 93.43 | $In_2O_3$ | none | 5.4 | 10.1369 |
| 12 | 10.93 | 91.08 | $In_2O_3$ | none | 4.9 | 10.1381 |
| 14 | 12.60 | 90.03 | $In_2O_3$ | none | 4.5 | 10.1392 |
| 16 | 14.41 | 90.05 | $In_2O_3$ | none | 4.2 | 10.1399 |
| 18 | 16.24 | 90.21 | $In_2O_3$ | none | 4.1 | 10.1414 |
| 20 | 18.03 | 90.17 | $In_2O_3$ | none | 4.1 | 10.1419 |

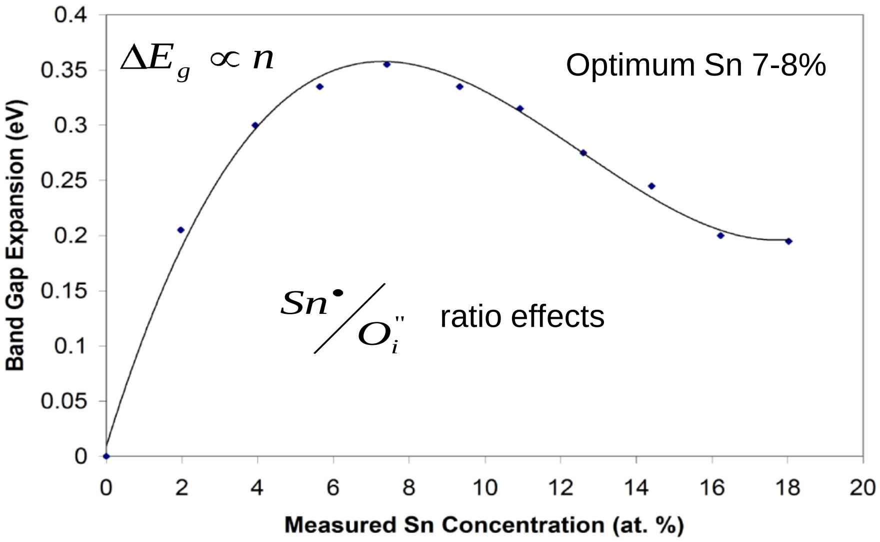


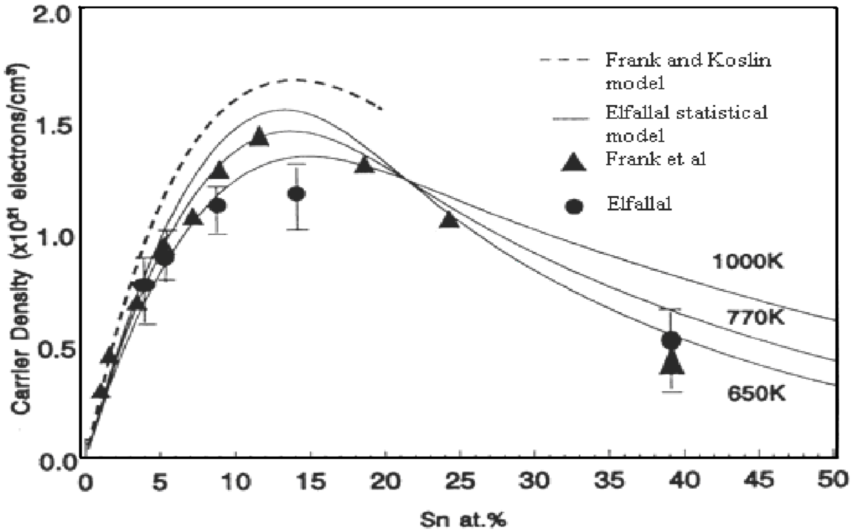



# System Optimization: Optical Effects



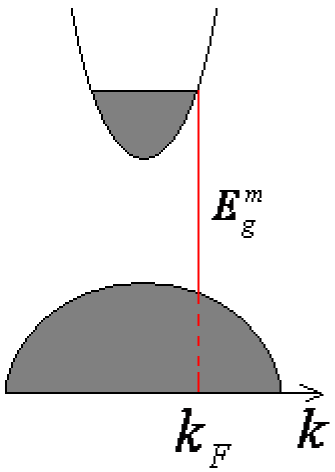

- Band gap for each colloidal dispersion determined with absorption coefficient.
- Concentration-dependent form of the Beer-Lambert law used.
- Optimum Sn conc. for colloidal ITO lower than that observed for typical thin films.




I. Elfallal, R. D. Pilkington, A. E. Hill, *Thin Solid Films* **1993**, *223*, 303.

# Potential Influence of Electron Confinement

## *Free CB Electron*

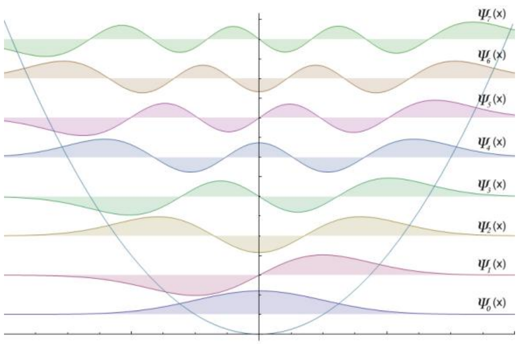



$$\Delta E_g^m = \frac{\hbar^2}{2m_{vc}^*}(3\pi^2 n)^{2/3} - \frac{e^2}{2\varepsilon_\infty \pi^2}(3\pi^2 n)^{1/3}$$

$$k_F = (3\pi^2 n)^{1/3}$$

Derived using classical Newtonian mechanics and the de Broglie wave nature. Based on momentum of the free electron.

## *Confined CB Electron*



Time-Independent Schrodinger

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

Solution within a confined box of length *L*

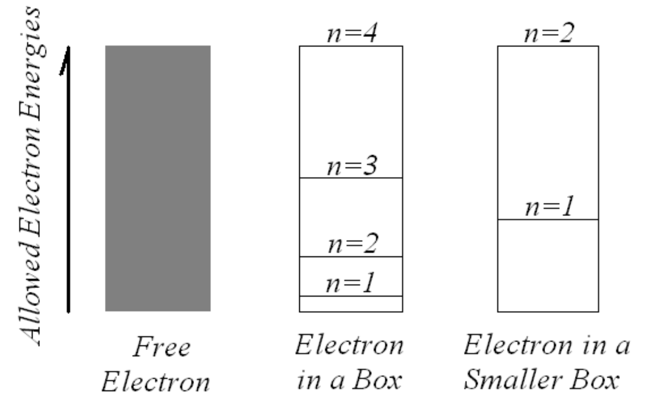
$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Only sine waves exist within and thus,

$$k = \frac{n\pi}{L}$$

# EMA Model of Electron Confinement in ITO

$$E_n = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m}\left[\frac{k}{2\pi}\right]^2 = \frac{n^2\hbar^2\pi^2}{2mL^2}$$




**Effective Mass Approximation**

$$E(R) = E_g + \frac{h^2\pi^2}{2R^2 m_{cv}^*} - \frac{1.8e^2}{\varepsilon_\infty R}$$

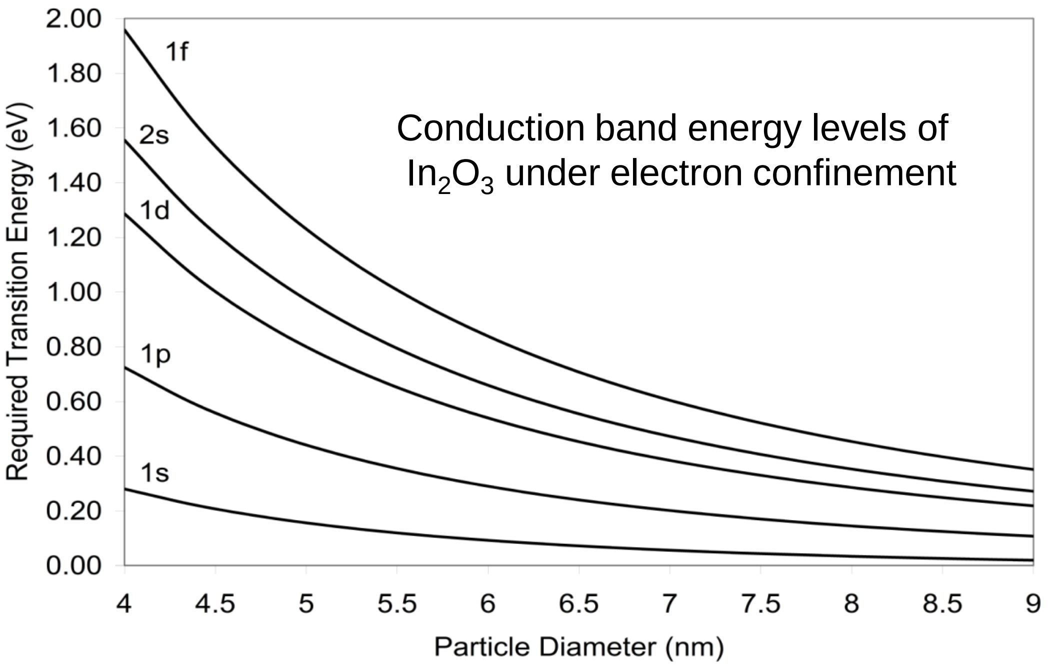
**Bohr Radius**

$$a_B = \frac{h^2\varepsilon_\infty}{\pi e^2}\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right) \cong 2.13nm\_(ITO)$$

**Spherical harmonics & Bessel Function**

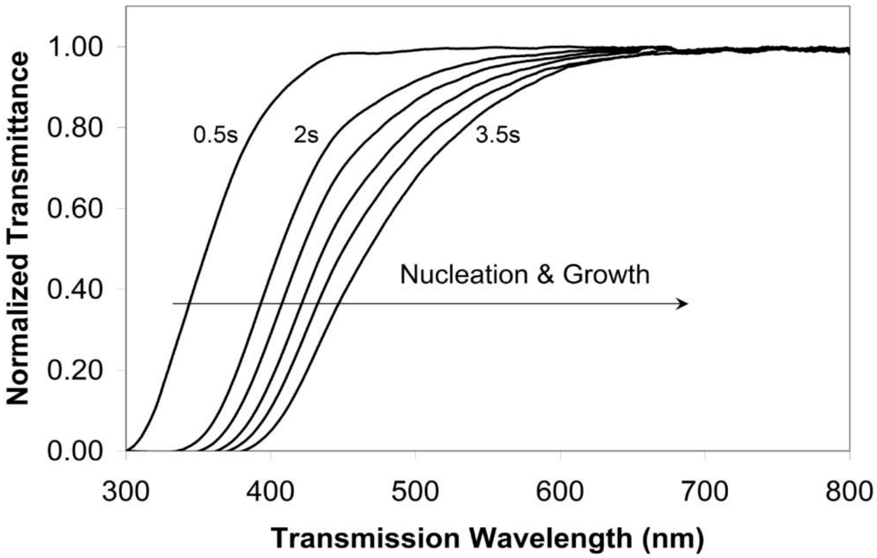
$$\psi(r) = \vartheta_l^m(\theta,\varphi)R(r)$$

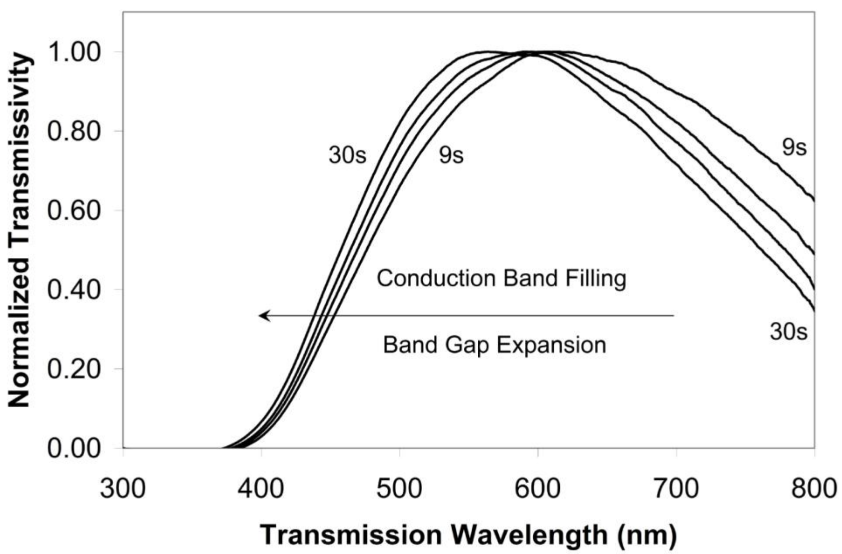
$$E_{nl} = \frac{2\hbar^2\chi_{nl}^2}{mD^2}$$

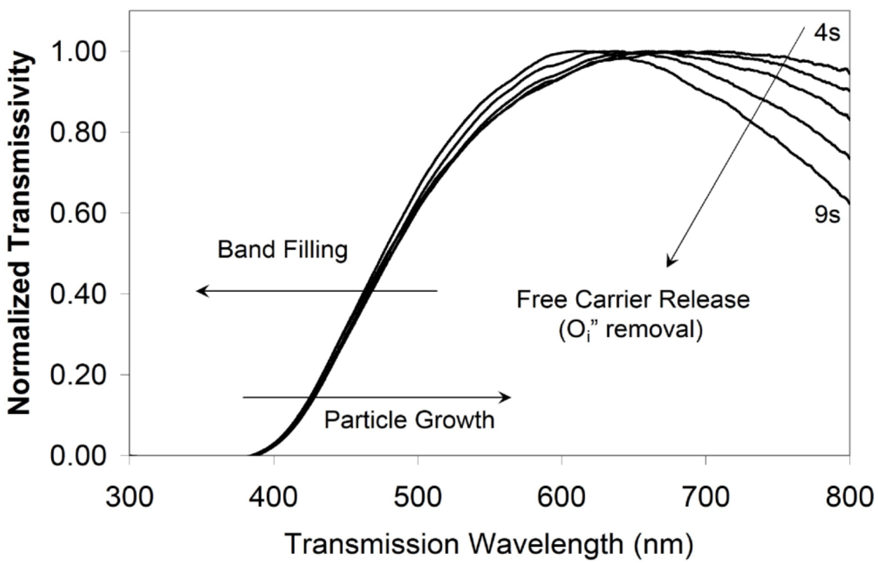


# Electron Generation: In-Situ Reaction Monitoring

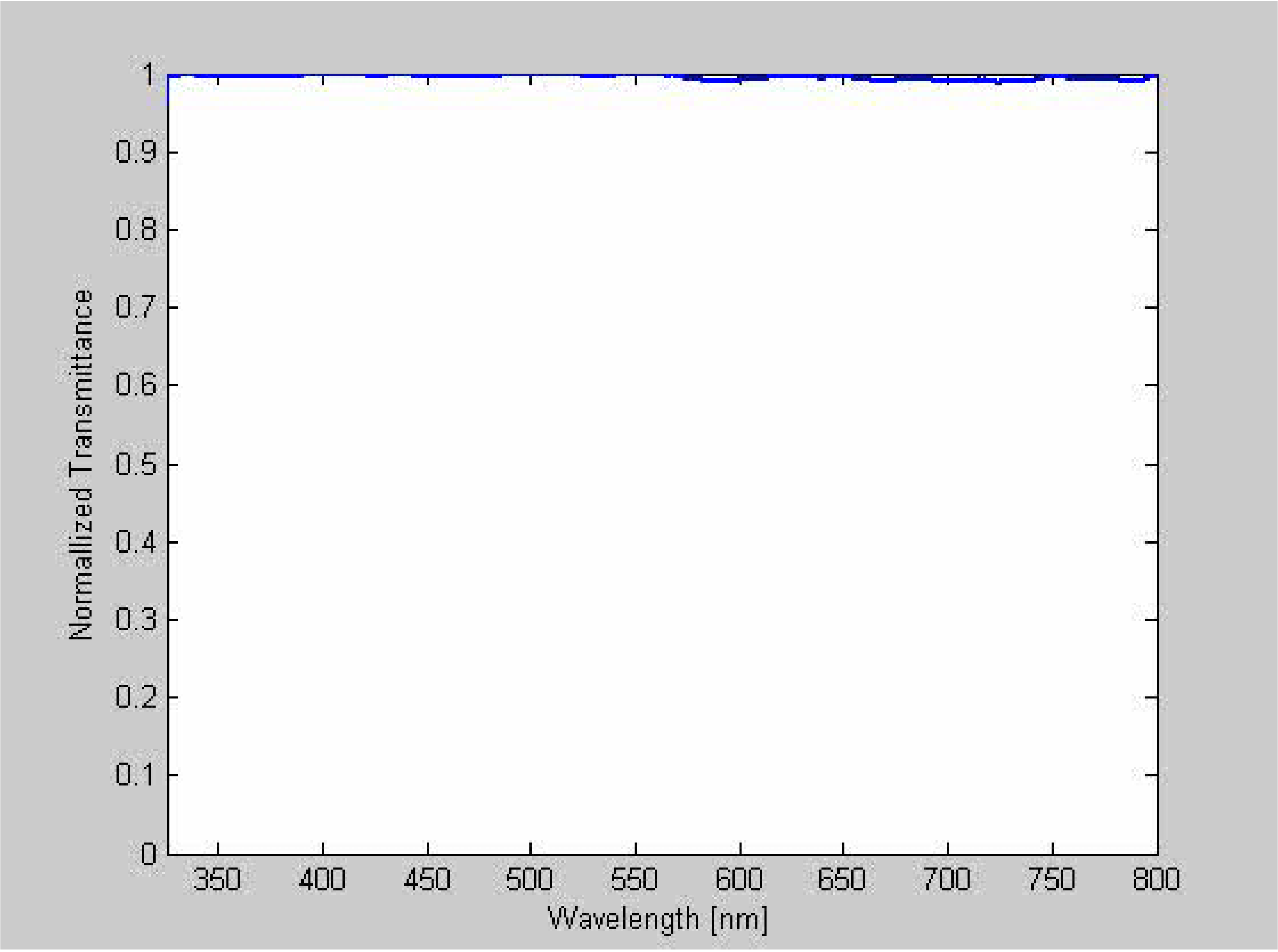
- Primary nucleation stage and Beer-Lambert effects within first 2 seconds.
- Particle growth (2-3.5s) moving from 100s to 1000s of atoms (decreased quantization)
- No further movement from 4 to 9 seconds while reflection edge forms.
- Growth + Band Filling
- Band gap expansion 9 to 30s



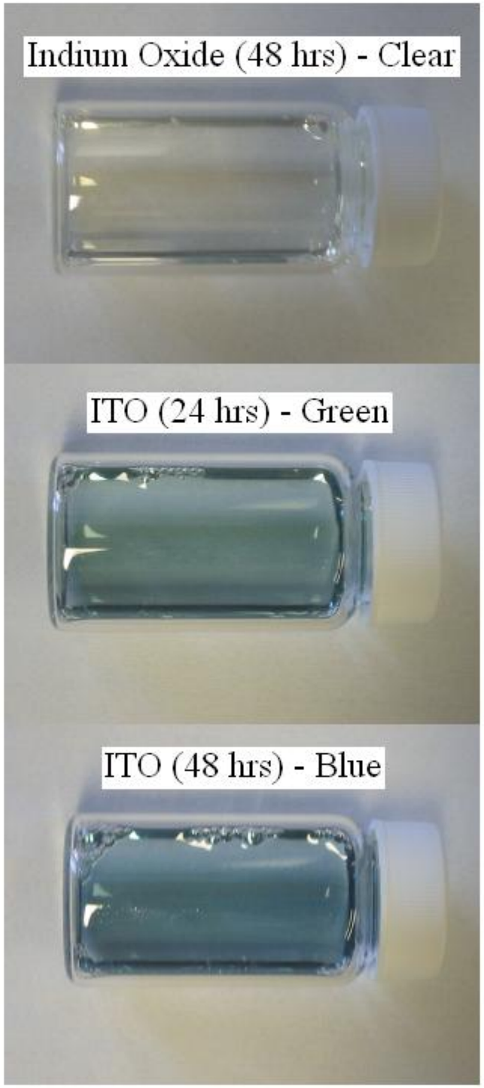



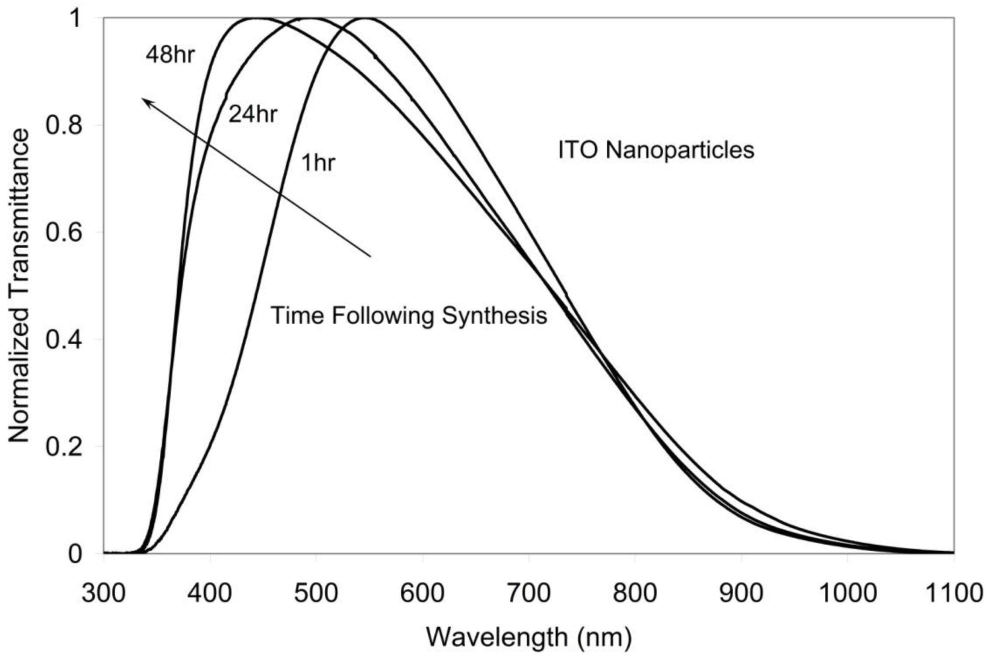
# In-Situ Analysis of Colloidal ITO Formation



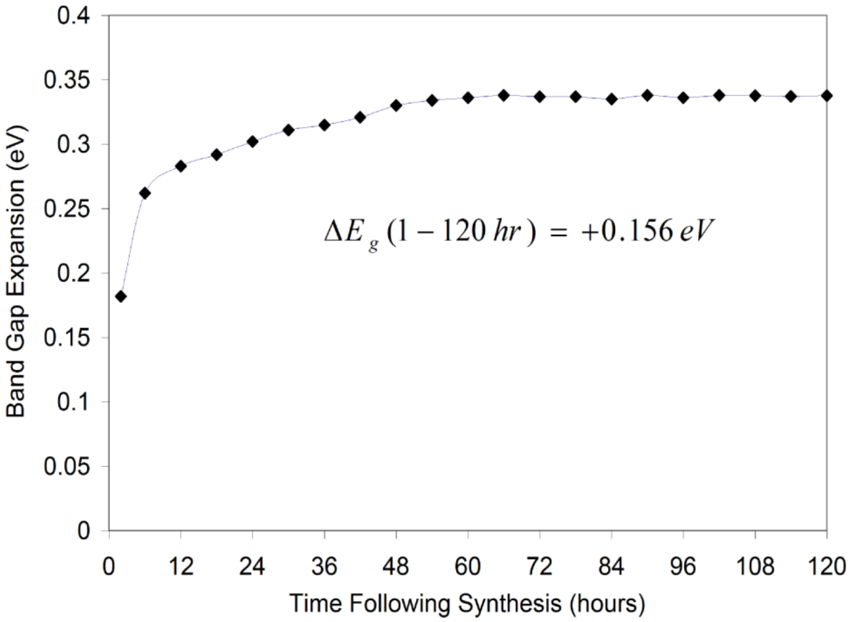
# Electron Generation: Band Filling Analysis I




- Continued spectral shift due to CB filling.
- Green to Blue body color change.
- Relatively slow rate offers an opportunity for analysis of band filling.
- Compare CB filling (Free vs. Confined)



# Electron Generation: Band Filling Analysis II




Est. ***free*** electron conc. at 120hr

$$n \approx 1.8\times10^{20}\,cm^{-3}$$

~14 electrons per particle

$$\Delta n \approx 9\times10^{19}\,cm^{-3}$$

~7e' added during analysis period

**Intrinsic ITO Parameters (Gupta 1989)**

$$(\varepsilon_\infty = 8.9\varepsilon_o, m_c^* = 0.35m_e, m_{vc}^* = 0.22m_e)$$

**Mott Critical Concentration (ITO)**

$$N_{c\cong} 5.62x10^{18}\,cm^{-3}\,\_(ITO)$$

**Resultant Band Gap Expansion**

$$\Delta E_g^{BM} = \frac{\hbar^2}{2m_{vc}^*}(3\pi^2 n)^{2/3} \cong 0.05eV$$

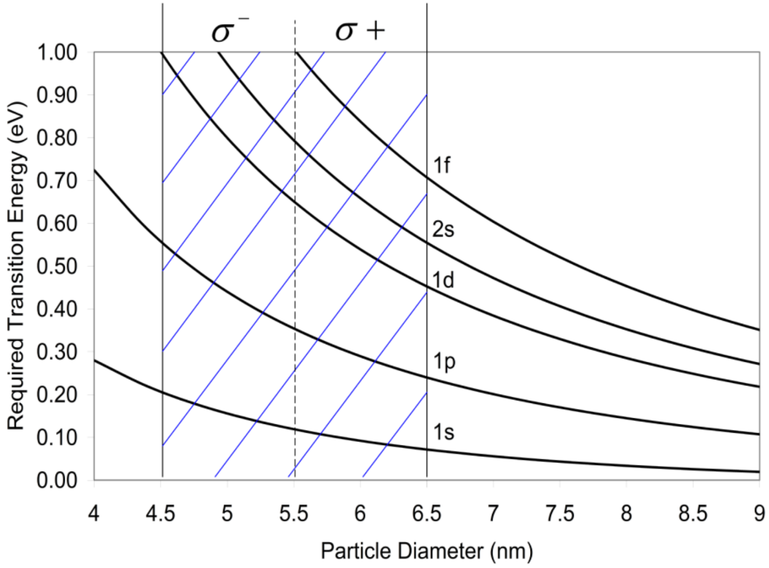
**First approximation (exchange interactions only)**

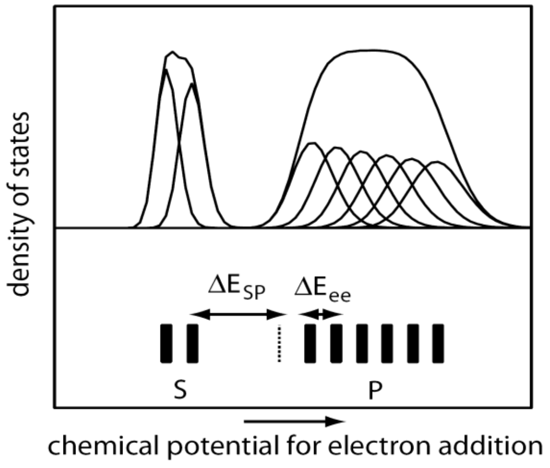
$$\Delta E_g = \frac{\hbar^2}{2m_{vc}^*}(3\pi^2 n)^{2/3} - \frac{e^2}{2\varepsilon_\infty \pi^2}(3\pi^2 n)^{1/3}$$

**Free-Carrier Concentration Estimate**

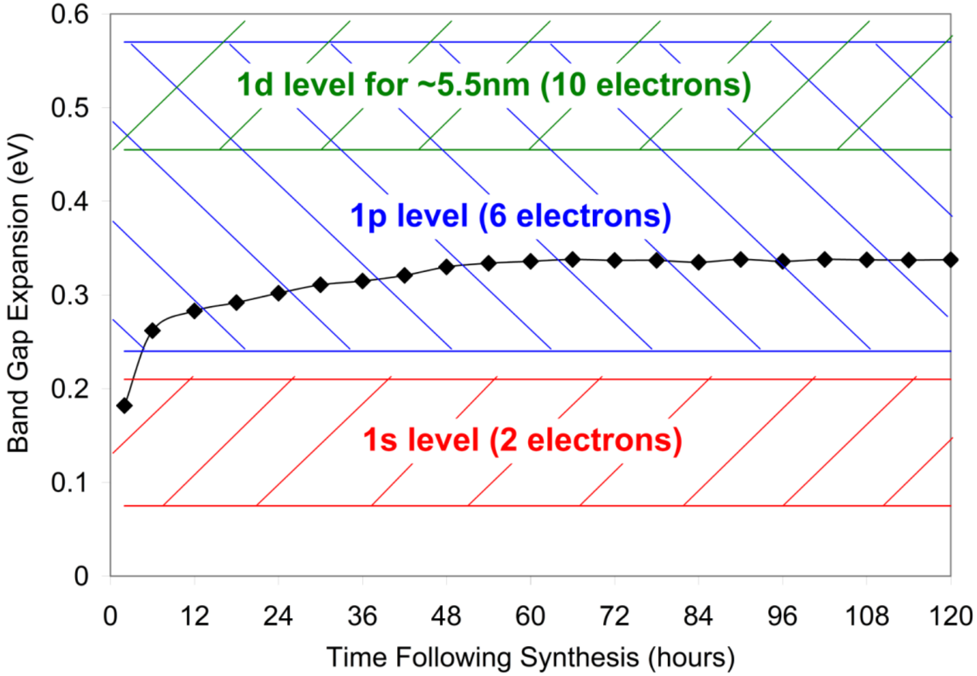
$$n \cong \frac{(m_{vc}^*)^3}{874.82\hbar^6}\left\{\frac{0.157e^2}{\varepsilon_\infty} + \sqrt{\left(\frac{0.157e^2}{\varepsilon_\infty}\right)^2 + 4\left(\frac{4.782\hbar^2}{m_{vc}^*}\right)\Delta E_g}\right\}^3$$

# Electron Generation: Band Filling Analysis III

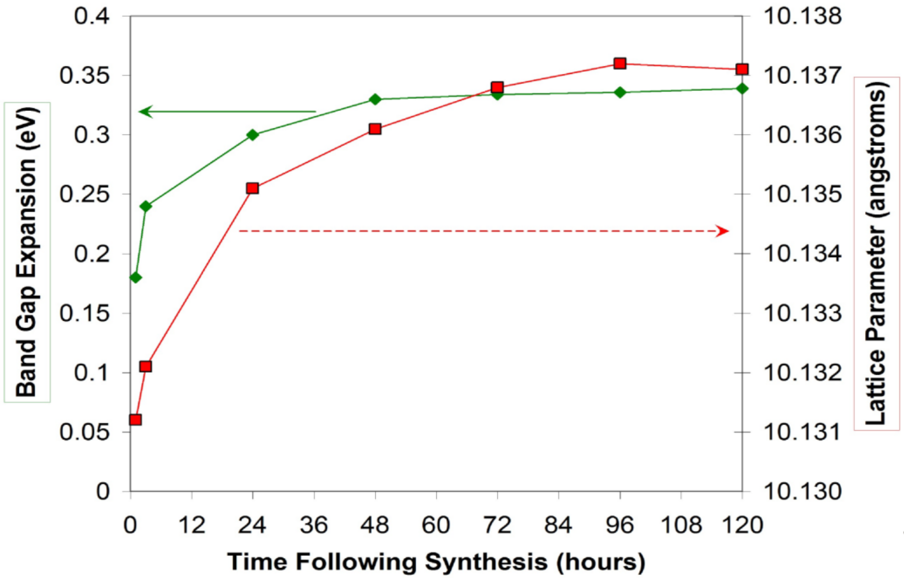


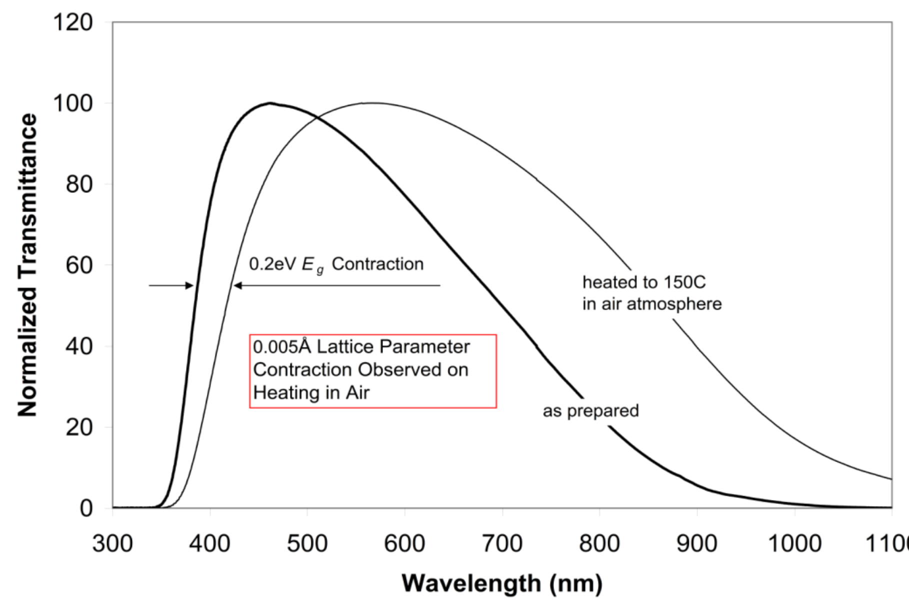

- Take into account particle size-distribution.
- EMA predicts ~8 ***confined*** electrons/particle are able to produce the measured expansion.
- EMA over-estimates and electron mass incr.
- 1d levels may have been reached.



# Electron Generation: Support for Frank & Kostlin

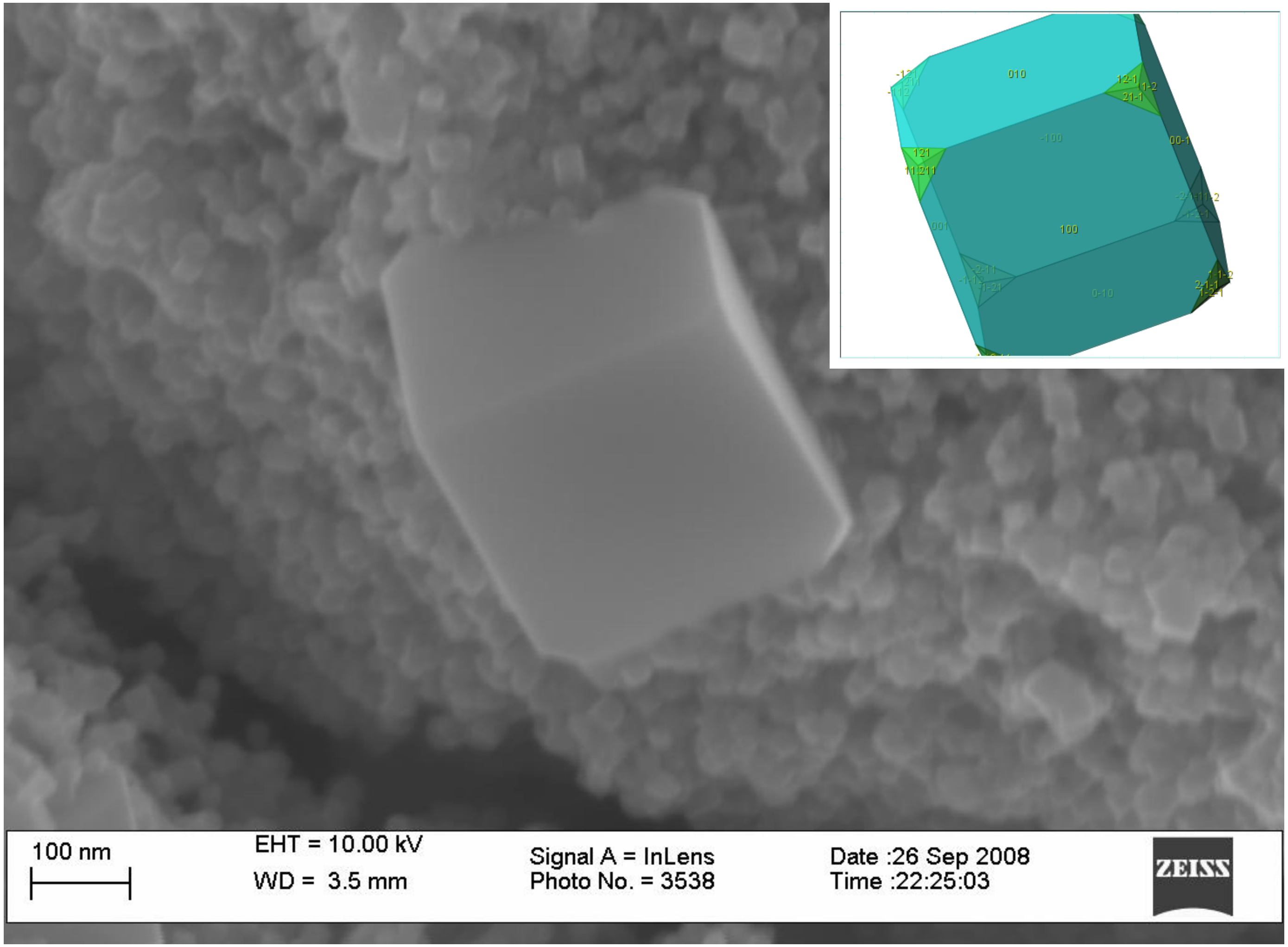



- ITO lattice expands due to electrostatic repulsion between *Sn** ⟷ *Sn** dopants.
- Interstitial oxygen should partially screen.
- Theorized that removal of $O_i''$ would be observed as a lattice parameter expansion.
- Correlates well with band gap expansion.




- Heat dispersion in air at 150C to oxide.
- Re-disperse in chloroform.
- Band gap contraction indicating loss of conduction band electron.
- Lattice parameter contraction may indicate return of interstitial oxygen.

# Extended Growth From Pressure Anneal



# Summary

- Rapid and cost-effective method to produce a stable dispersion of colloidal ITO nanoparticles has been developed.
- Particles are pure phase, ~5-7nm in diameter, and display an essentially single-crystalline character.
- System forms a non-agglomerated, optically clear solution and can remain in this state for months/years.
- Optical analysis indicates the intrinsic free electron concentration is on the order of $1.8 \times 10^{20}$ $cm^{-3}$ or higher.
- Monitoring the generation of free electrons on different time scales (milliseconds to hours) allowed particle formation, conduction band filling, and the very origin of conductivity in ITO to be probed.
- A large volume reaction technique has been developed to promote industry adoption of this material form.