



Optical Properties of Materials

ISSUES TO ADDRESS...

- What happens when light shines on a material?
- Why do materials have characteristic colors?
- Why are some materials transparent and others not?
- Optical applications:
 - luminescence
 - photoconductivity
 - solar cell
 - optical communications fibers

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Optical Properties

Light has both particulate and wavelike properties: Photons

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

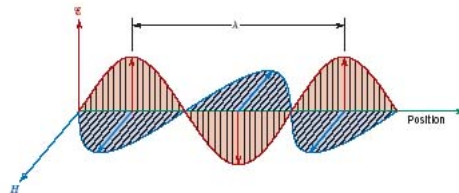
ΔE = energy

λ = wavelength

ν = frequency

h = Planck's constant (6.62×10^{-34} J · s)

c = speed of light (3.00×10^8 m/s)




λ for visible light: 400 nm (blue) to 800 nm (red)

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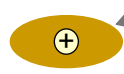
Refractive Index, n

- Transmitted light distorts electron clouds.

no transmitted light



transmitted light

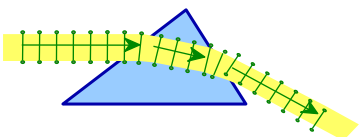


← electron cloud distorts

Polarizable ions (e.g., lead) are most effective in decreasing the speed of light.
- Light is slower in a material vs vacuum.

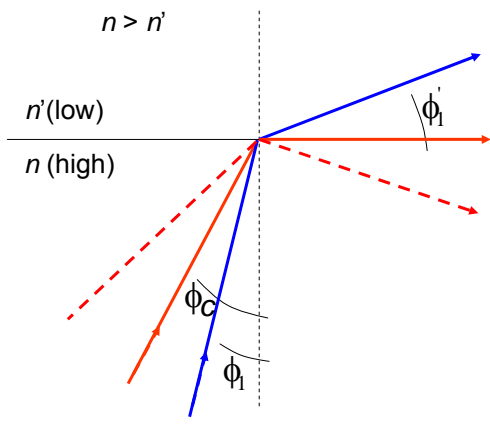
$n = \text{refractive index} \equiv \frac{c \text{ (velocity of light in vacuum)}}{v \text{ (velocity of light in medium)}}$

Typical glasses ca.	1.5 -1.7
Plastics	1.3 -1.6
PbO (Litharge)	2.67
Diamond	2.41


- Note: n is a function of the wavelength of light

Total Internal Reflectance

$n > n'$



$$\frac{n}{n'} = \frac{\sin \phi'}{\sin \phi}$$

ϕ_i = incident angle
 ϕ_r = refracted angle
 ϕ_c = critical angle

ϕ_c occurs when $\phi_r = 90^\circ$
 for $\phi_i > \phi_c$ light is internally reflected



Example: Diamond in air

$$\frac{n}{n'} = \frac{\sin \phi'}{\sin \phi} \Rightarrow \frac{2.41}{1} = \frac{\sin 90^\circ}{\sin \phi_c} = \frac{1}{\sin \phi_c}$$

$$\sin \phi_c = \frac{1}{2.41}$$

$$\phi_c = 24.5^\circ$$

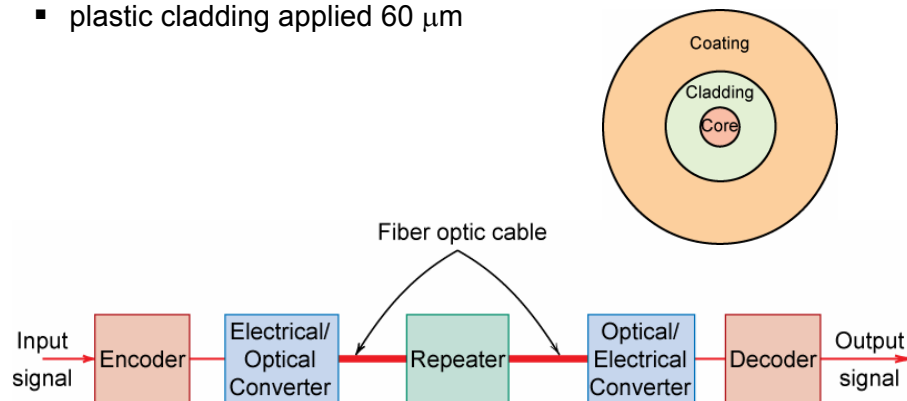
- Fiber optic cables are clad in low n material for this reason.

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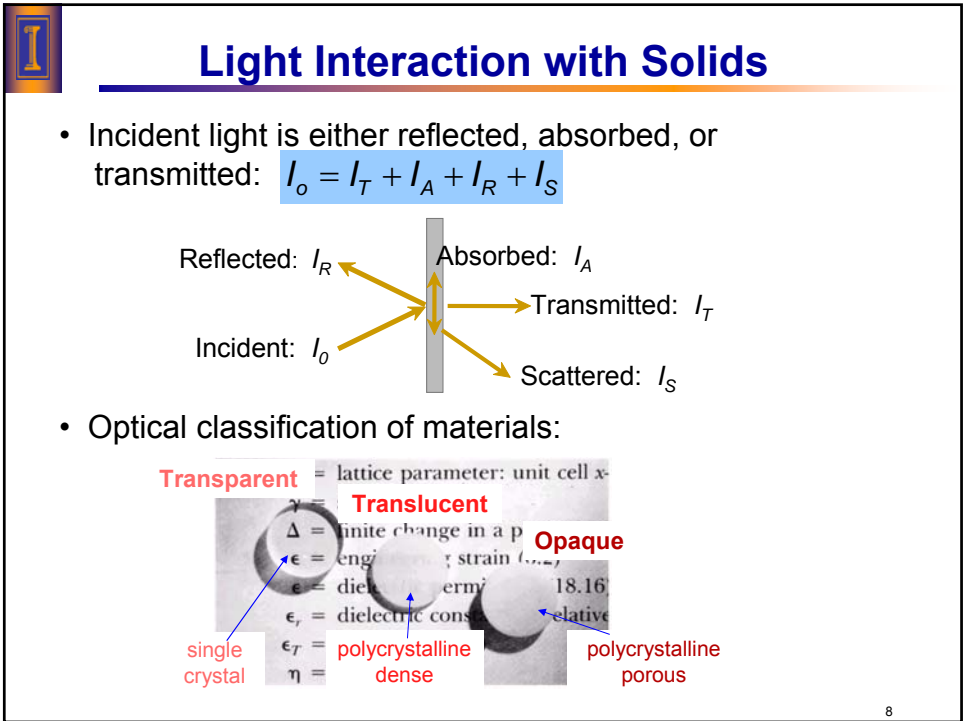
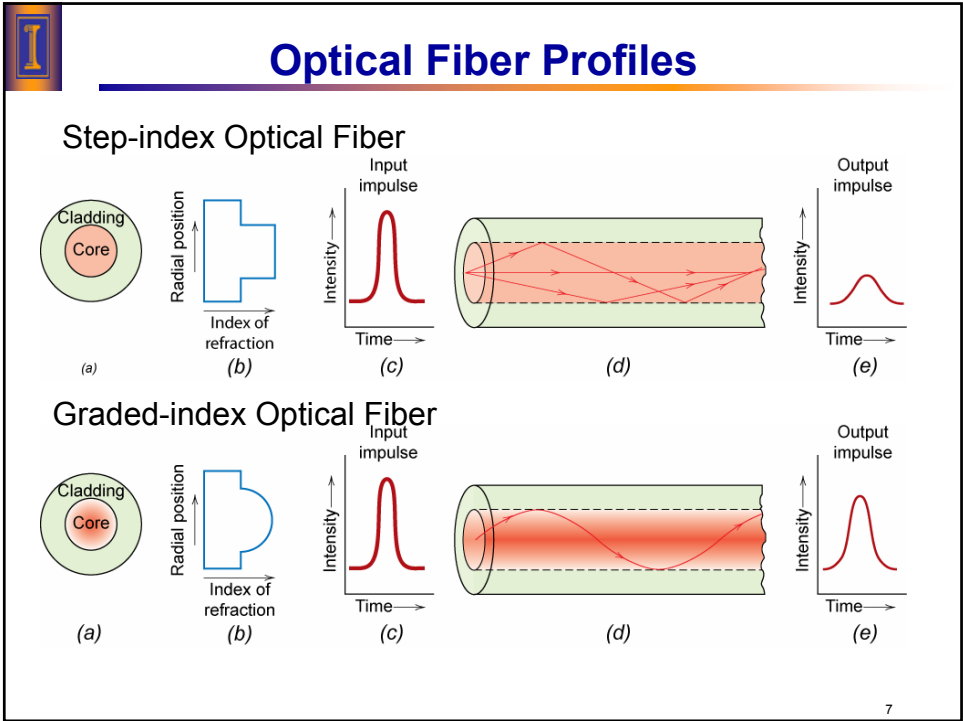


Optical Fibers

- prepare preform by extrusion
- preform drawn to 125 μm or less capillary fibers
- plastic cladding applied 60 μm



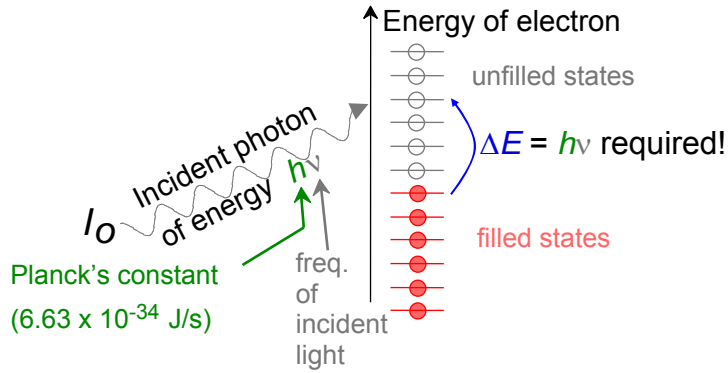
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Optical Properties of Metals: Absorption

- Absorption of photons by electron transition:



- Metals have a fine succession of energy states.
- Near-surface electrons absorb visible light.

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Light Absorption

$$\frac{I}{I_0} = e^{-\alpha t} \quad \alpha = \text{linear absorption coefficient [cm}^{-1}\text{]}$$

$t = \text{sample thickness}$

$$\ln \left[\frac{I}{I_0} \right] = -\alpha t$$

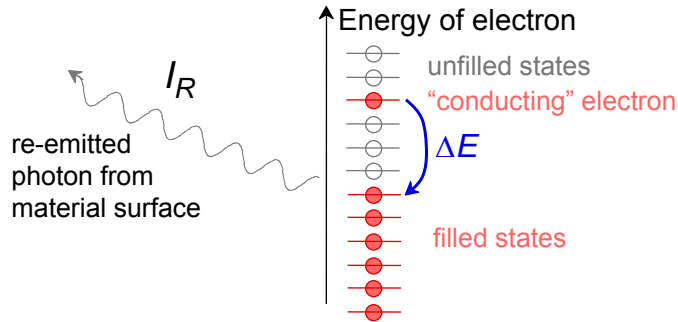
Beer's Law: $A = \epsilon l C$

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Optical Properties of Metals: Reflection

- **Electron transition** emits a photon.



- **Reflectivity** = I_R/I_0 is between 0.90 and 0.95.
- Reflected light is same frequency as incident.
- Metals appear reflective (shiny)!

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Reflectivity, R

- **Reflection**

Metals reflect almost all light

Copper & gold absorb in blue & green => gold color

$$R = \left(\frac{n-1}{n+1} \right)^2 = \text{reflectivity}$$

- Example: Diamond $R = \left(\frac{2.41-1}{2.41+1} \right)^2 = 0.17$

∴ 17% of light is reflected

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Scattering

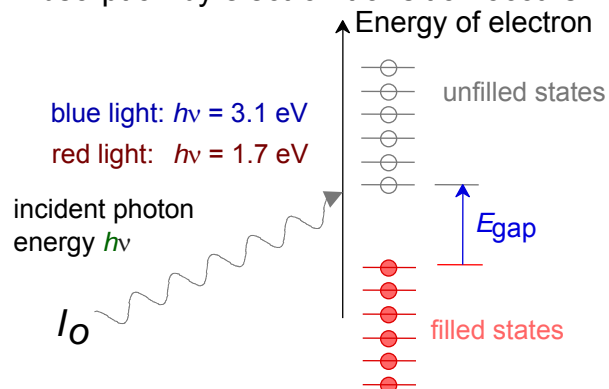
- Occurs especially in semicrystalline & polycrystalline materials
- Semicrystalline – mixture of crystalline and amorphous phases**
 - density of crystals higher than amorphous materials
 - \therefore speed of light is lower
 - causes light to change direction = scatter
 - can cause significant loss of light during transmission
- Common in polymers
 - Ex: Polyethylene milk bottles – cloudy because of crystalline regions
 - Plexiglass (polymethylmethacrylate) – clear – essentially no crystals

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Selected Absorption: Semiconductors

- Absorption by electron transition occurs if $h\nu > E_{\text{gap}}$



- If $E_{\text{gap}} < 1.8 \text{ eV}$, full absorption; color is black (Si, GaAs)
- If $E_{\text{gap}} > 3.1 \text{ eV}$, no absorption; colorless (diamond)
- If E_{gap} in between, partial absorption; material has a color.

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Wavelength vs. Band Gap

e.g.: What is the minimum wavelength absorbed by Ge?

$$E_g = 0.67 \text{ eV}$$

$$\lambda_c = \frac{hc}{E_g} = \frac{(6.62 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^8 \text{ m/s})}{(0.67 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} \leq 1.85 \mu\text{m}$$

$$1.85 \mu\text{m} = 1850 \text{ nm} = 18,500 \text{ \AA} = 5400 \text{ cm}^{-1} = \text{infrared}$$

note: for Si $E_g = 1.1 \text{ eV}$ $\lambda_c \leq 1.13 \mu\text{m}$

If donor (or acceptor) states also available, this provides other absorption frequencies

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Color of Nonmetals

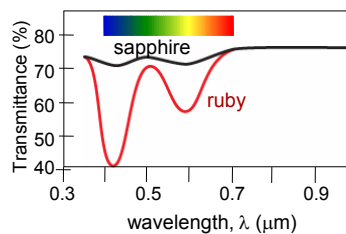
- Color determined by sum of frequencies of transmitted light + re-emitted light from electron transitions.
- Ex: Cadmium Sulfide (CdS)
 $E_{gap} = 2.4 \text{ eV} = 516 \text{ nm} = 5160 \text{ \AA} = \text{green}$
absorbs higher energy visible light (blue, violet),
Red/yellow/orange is transmitted and gives it color.
- Ex: **Ruby** = Sapphire (Al_2O_3) + (0.5 to 2) at% Cr_2O_3

Sapphire is colorless

(i.e., $E_{gap} > 3.1 \text{ eV}$)

adding Cr_2O_3 :

- alters the band gap
- blue light is absorbed
- yellow/green is absorbed
- red is transmitted
- Result: **Ruby** is deep red in color.

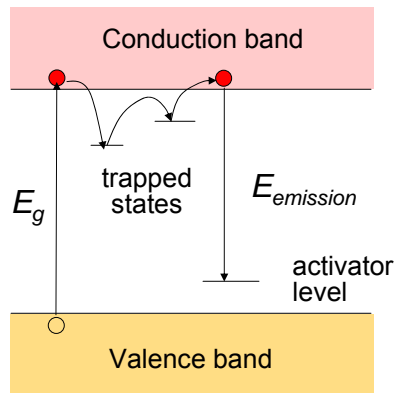


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Luminescence

- **Luminescence** – emission of light by a material
material absorbs light at one frequency & emits at another (lower) frequency.



How stable is the trapped state?

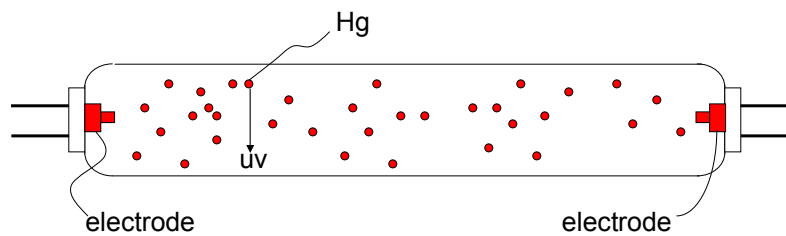
- If very stable (long-lived = $>10^{-8}$ s) = **phosphorescence**
- If less stable ($<10^{-8}$ s) = **fluorescence**

Example: glow in the dark toys.
Charge them up by exposing them to the light. Reemit over time.
phosphorescence

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Photoluminescence



- Arc between electrodes excites mercury in lamp to higher energy level.
- Electron falls back emitting UV light (i.e., suntan lamp).
- Line inner surface with material that absorbs UV, emits visible



Sb^{3+} blue

Mn^{2+} orange-red

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Cathodoluminescence

- Used in T.V. set
 - Bombard phosphor with electrons
 - Electrons excite phosphor to high state
 - Excited state relaxed by emitting photon (visible)
 - ZnS, doped with Ag⁺ + Cl⁻ blue**
 - (Zn,Cd)S, doped with Cu⁺⁺ Al³⁺ green**
 - Y₂O₂S, doped with 3% Eu red**
- Note: light emitted is random in phase & direction
i.e., noncoherent

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Laser Light

- Non-coherent light diverges and can't be tightly collimated
- How could we get all the light in phase? (coherent)
 - LASERS**
 - Light**
 - Amplification by**
 - Stimulated**
 - Emission of**
 - Radiation**
- Involves a process called **population inversion** of energy states

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Population Inversion

- What if we could increase most species to the excited state?

The diagram illustrates the energy levels and transitions for a Cr^{3+} ion. The vertical axis represents Energy. The ground state is labeled G and is identified as Cr^{3+} . The excited state is labeled E . A dashed blue arrow shows a transition from E to a level labeled M , which is identified as the Metastable state. This transition is labeled "Spontaneous decay (nonradiative, phonon emission)". From the metastable state M , a solid blue arrow points down to the ground state G , labeled "Spontaneous and stimulated emission". A red wavy arrow labeled "Incident photon (xenon lamp)" points from the ground state G up to the excited state E , labeled "Electron excitation". A red wavy arrow labeled "Laser photon" points from the metastable state M down to the ground state G .

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Laser Light Production

- "pump" the lasing material to the excited state
e.g., by flash lamp (non-coherent lamp).

The diagram shows a schematic of a laser setup. A central orange cylinder represents the Ruby crystal. It is surrounded by a green helical coil labeled "Flash lamp". Below the flash lamp is a circuit diagram with a battery symbol and a switch, labeled "Power source". A red arrow labeled "Coherent beam" points to the right, emerging from the end of the Ruby crystal.

– If we let this just decay we get no coherence.

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Laser Cavity

“Tuned” cavity:

- **Stimulated Emission**
 - One photon induces the emission of another photon, in phase with the first.
 - cascades producing very intense burst of coherent radiation.
- i.e., **Pulsed laser**

The diagram illustrates the operation of a laser cavity in five stages:

- (a) A crystal with a fully silvered left end and a partially silvered right end. Excited Cr atoms (blue dots) are present in the crystal.
- (b) A photon is emitted from an excited atom, stimulating other excited atoms to emit photons in phase with it.
- (c) The photon cascade continues, with some photons being reflected back into the crystal.
- (d) The process is shown at three points: (Just before next reflection), (At midcrystal), and (After reflection), showing the increasing intensity of the photon burst.
- (e) The final stage shows a very intense burst of coherent radiation exiting through the partially silvered end.

Legend:
 ● Excited Cr atom
 ○ Cr atom in ground state

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Continuous Wave Lasers

- Can also use materials such as CO₂ or yttrium-aluminum-garnet (YAG) for lasers
- Set up standing wave in laser cavity – tune frequency by adjusting mirror spacing.
- Uses of CW lasers
 - Welding**
 - Drilling**
 - Cutting – laser carved wood, eye surgery**
 - Surface treatment**
 - Scribing – ceramics, etc.**
 - Photolithography – Excimer laser**

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Uses of Semiconductor Lasers

- #1 use = CD & DVD players
 - Color? - red Blue-Ray? - blue (duh)
- Banks of these semiconductor lasers are used as flash lamps to pump other lasers
- Communications
 - Fibers often turned to a specific frequency (typically in the blue)
 - only recently was this attainable

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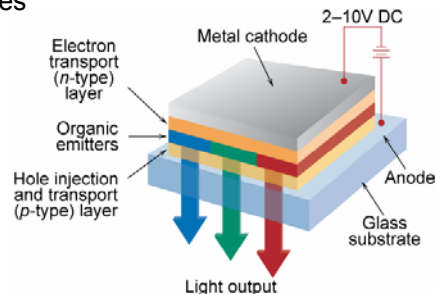


Applications of Materials Science

- New materials must be developed to make new & improved optical devices.

Organic Light Emitting Diodes (OLEDs)

White light semiconductor sources



- New semiconductors
- Materials scientists (& many others) use lasers as tools.
- Solar cells

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Solar Cells

- p-n* junction:**
- Operation:**
 incident photon produces hole-elec. pair.
 typically 0.5 V potential.
 current increases w/light intensity.
- Solar powered weather station:**

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Spatial Separation of Hole-Electron Pairs

How to prevent recombination of photogenerated electrons and holes?
 Usually accomplished by band bending, e.g., p-n heterojunction:

before contact

**after contact:
band bending**

**after photon:
spatial charge separation**

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Grand Challenge: "Solar-Power Paint"

Solar-Driven Photocatalytic Water Splitting:

There remain critical unsolved materials challenges before any practical device.

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Past History of Photochemical Water Splitting

Class of Device	Description	Limitations & Unsolved Problems
Small Band Gap Semiconductor-Solution Heterojunctions	35 years of effort. Band gap tuning via soln. potential.	Corrosion limited (even Si). No robust resolution.
Dye Sensitization	Very powerful for light harvesting. I_3^-/I^- relatively robust.	Dyes die after 10^8 photons. Very corrosive in practice.
Composite Devices/ Hybrid Photoelectrodes	WO_3 or Fe_2O_3 / Si multilayer.	Modest Quantum Yield. Usually requires applied potential. Often stability issues.
Oxide p-n Heterojunctions	First proposed by Nozik. Oxide-Sulfides/Se mostly (Kamat, Lee, ...).	Long neglected. S/Se corrosion limited. Light harvesting problematic.
Nanocluster catalysts (post-charge separation)	Pt / RuO_2 for H_2 & O_2 production. Works reasonably well.	Expensive.

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Pt / Titania Nanocomposites

Pt/TiO ₂	7.7
Pd/TiO ₂	6.7
Rh/TiO ₂	2.8
Ru/TiO ₂	0.2
Sn/TiO ₂	0.2
Ni/TiO ₂	0.1
TiO ₂	<0.1

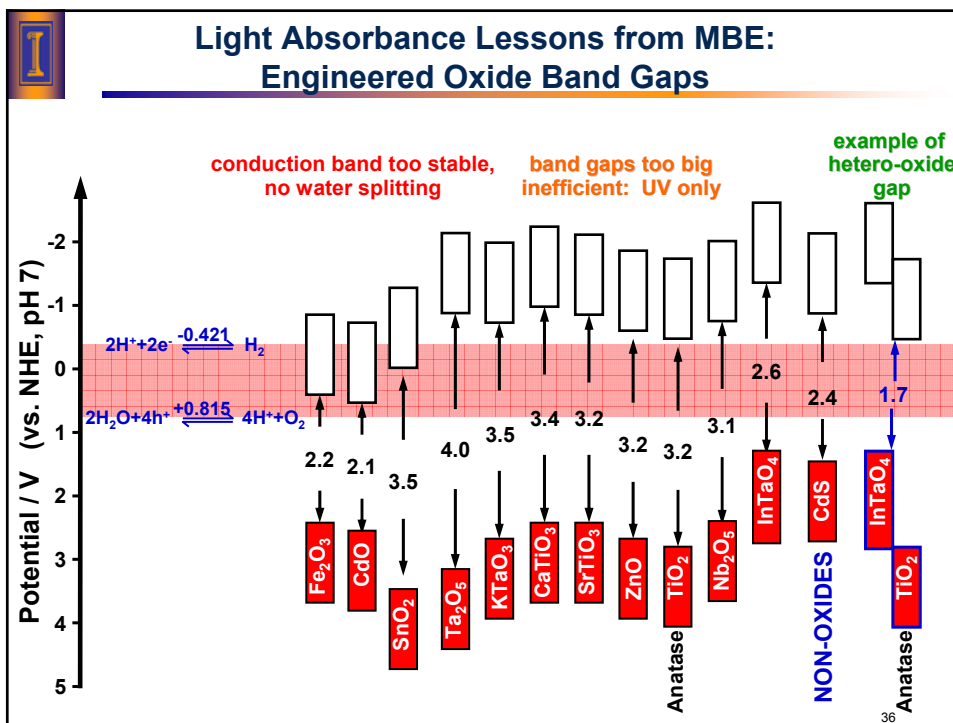
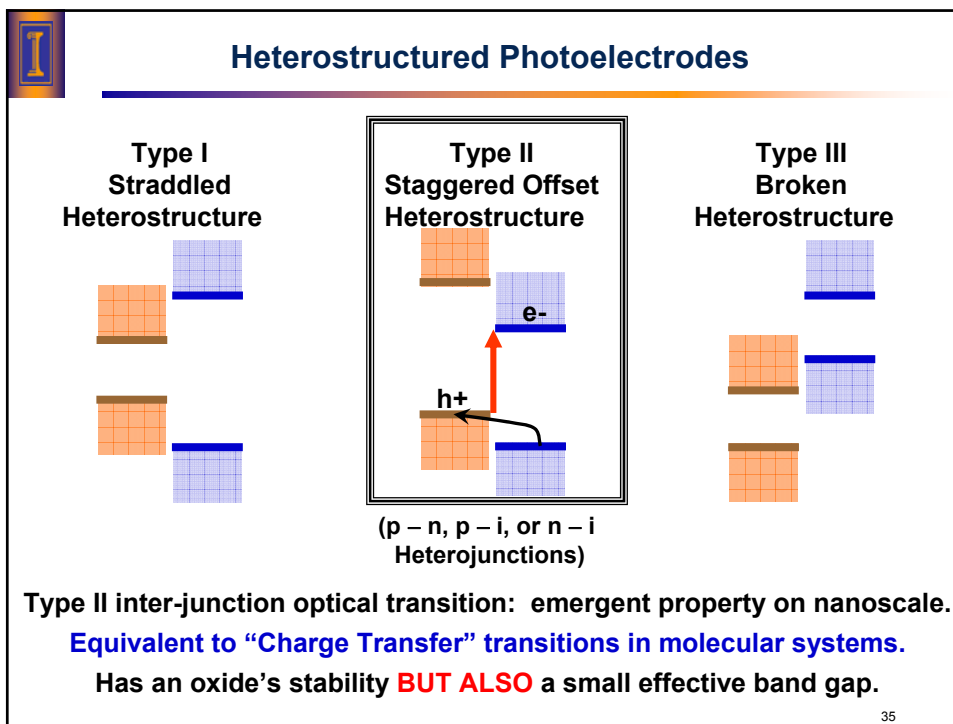
Toshima, J. Phys. Chem. 1985, 89, 1902

Cf. also: Subramanian, V.; Wolf, E. E.; Kamat, P. V. *J. Am. Chem. Soc.* 2004, 126, 4943.

Key Issues in Photochemical Water Splitting

- Existing Systems: Almost completely Metal Sulfides/Selenides (due to visible light absorption).
- Critical Problem: **Long term stability of photocatalysts.** Most semiconductors are NOT long-term stable in water during photolysis.
- Potential solution: Oxides are the thermodynamically stable state, **but** most oxides do not absorb visible light.
- What is needed: Band gap engineering of **Oxide-Oxide Interfaces** to create new absorbance mechanisms.

This is an exploratory materials effort, not a device project.



Digital Superlattice for Band Structure Engineering

Eckstein

Goal: Create new visible absorption by staggered Type-2 oxide heterojunctions. Requires *high density* of red-ox active interfaces.

red-ox
oxide
heterojunction

ABO_3 CDO_3

$SrTiO_3$ $LaMnO_3$
 $SrMnO_3$ $LaScO_3$
 $SrCrO_3$ $LaNiO_3$
 $SrCoO_3$ KVO_3

Lateral SL by
MBE step-
flow growth:

50-100 nm

Vertical SL
by multi-
layer MBE:

$SrTiO_3$ $LaMnO_3$

New Abs.

New valence-to-conduction band transition: solid-state analog to molecular Charge-Transfer transitions.

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Complex Interfacial 'Designer' Structures

Eckstein, Zuo with Wen, Petrov (FS-MRL staff)

LMO →

LMO →

LMO →

LMO →

Z-contrast image

Ti Mn La O

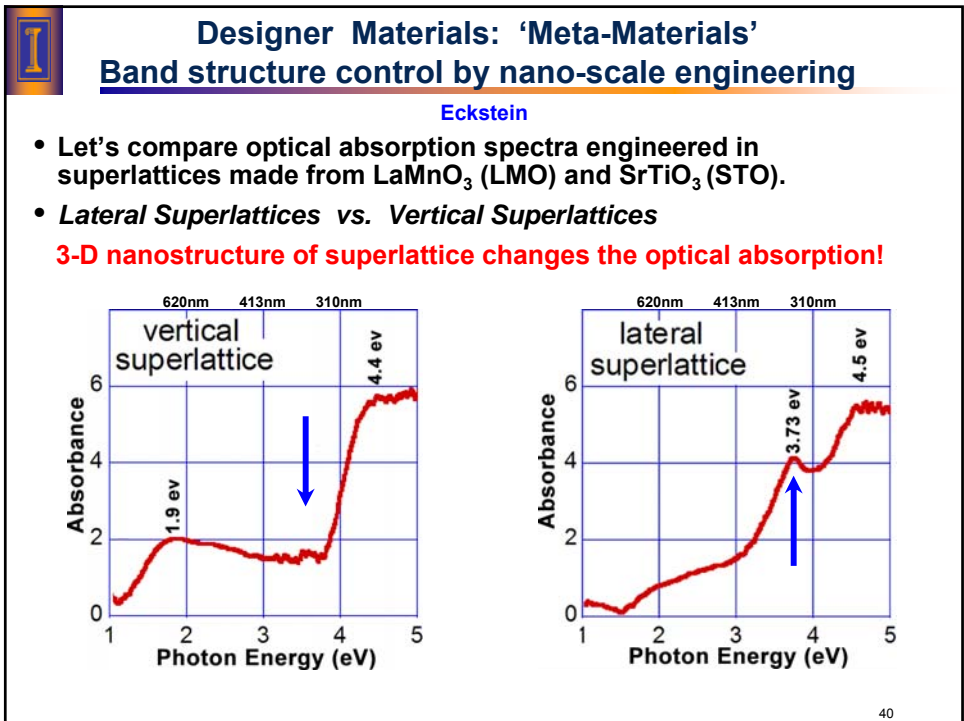
L_{23} L_{23} M_{45} K-edge

EELS line scan

Electron Energy-loss Spectrum

STO = $SrTiO_3$
 SMO = $SrMnO_3$
 LMO = $LaMnO_3$

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SUMMARY

- When light (radiation) shines on a material, it may be: **reflected**, **absorbed** and/or **transmitted**.
- Optical classification: **transparent**, **translucent**, **opaque**
- Metals:
fine succession of energy states causes absorption and reflection.
- Non-Metals:
may have *full* ($E_{gap} < 1.8\text{eV}$), *no* ($E_{gap} > 3.1\text{eV}$), or *partial* absorption ($1.8\text{eV} < E_{gap} = 3.1\text{eV}$).
color is determined by light wavelengths that are transmitted or re-emitted from electron transitions.
color may be changed by adding impurities which change the band gap magnitude (e.g., **Ruby**)
- **Refraction**:
speed of transmitted light varies among materials.