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Cathodolumiescence Studies of the Density of States of Disordered Silicon Dioxide

JR Dennison
Utah State Univesity

Amberly Evans Jensen

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Cathodolumiescence Studies of the Density of States of Disordered Silicon Dioxide

JR Dennison and Amberly Evans Jensen

Materials Physics Group
Physics Department
Utah State University

Talk B2.00004

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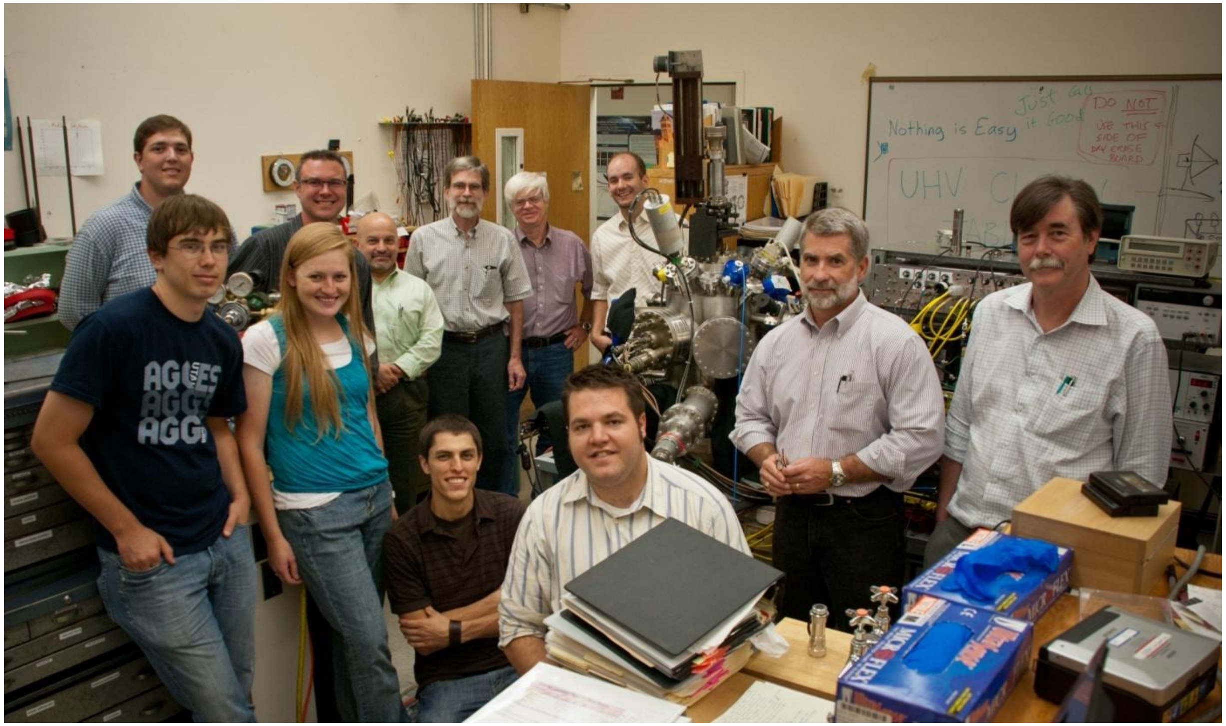
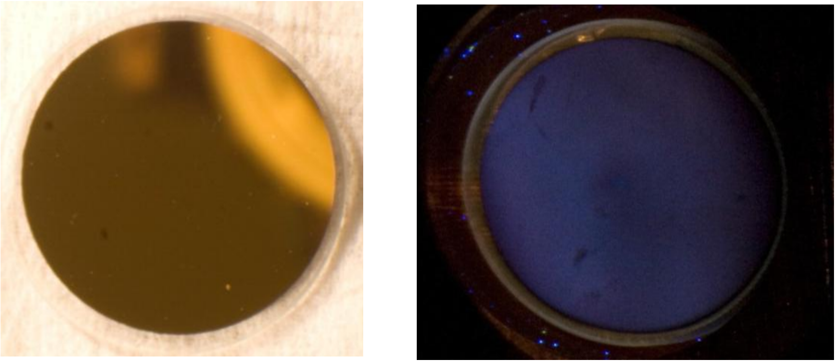


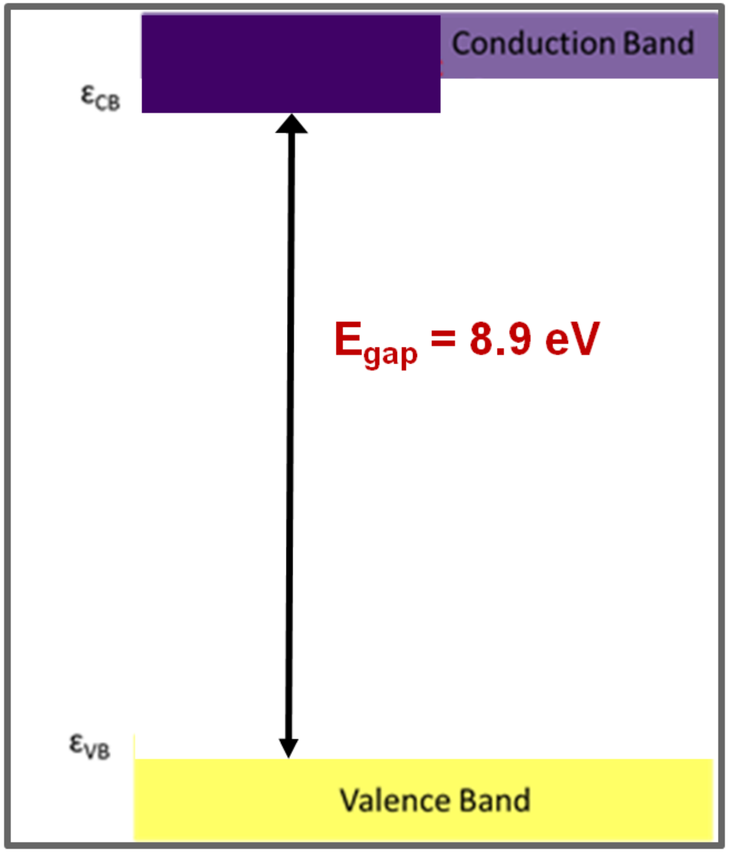
USU Materials Physics Group

Disordered SiO_2--a Common Spacecraft Material



- Original study of electron-induced luminescence--or cathodoluminescence (CL)--of thin film fused silica (highly disordered SiO_2) originally motivated by “pollution” an optical coating on mirrors located on space-based observatories [Christensen, D-004 and Zia F1.016].

- A great deal can be learned about the electronic band structure of fused silica by studying the behavior of its CL.



Optical Transmission Data:

- Direct band gap ~8.9 eV
- Additional steps in transmission in 1-4 eV range

Cathodoluminescence—Deep and Shallow Trap DOS

Cathodoluminescence intensity (α emitted power)

$$I_\gamma(J_b,E_b,T,\lambda) \propto \frac{\dot{D}(J_b,E_b)}{\dot{D}+\dot{D}_{sat}}\{[1-e^{-(\varepsilon_{ST}/k_BT)}]\}\{[1-\mathbb{A}_f(\lambda)][1+\mathbb{R}_m(\lambda)]\}$$

Dose rate (α adsorbed power)

$$\dot{D}(J_b,E_b)=\frac{E_b\,J_b[1-\eta(E_b)]}{q_e\rho_m}\times\begin{cases}[1/L] & ;\,R(E_b)<L\\ [1/R(E_b)] & ;\,R(E_b)>L\end{cases}$$

J_b: incident current density
E_b: incident beam energy
q_e: electron charge
L: Sample thickness
ε_{ST}: shallow trap energy
$\eta(E_b)$: backscatter yield

T: temperature
λ: photon wavelength
ρ_m: mass density
D_{sat}: saturation dose rate
$R(E_b)$: penetration range

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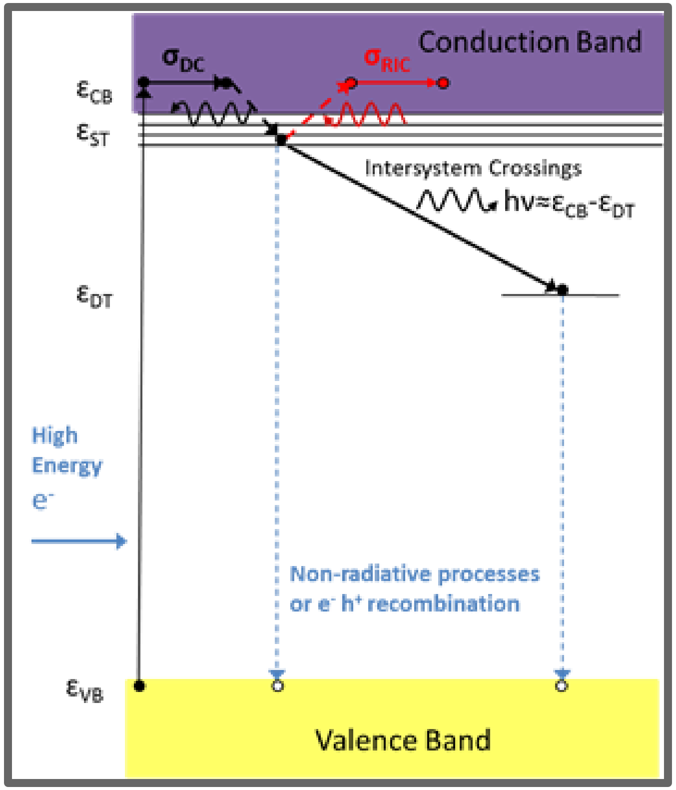
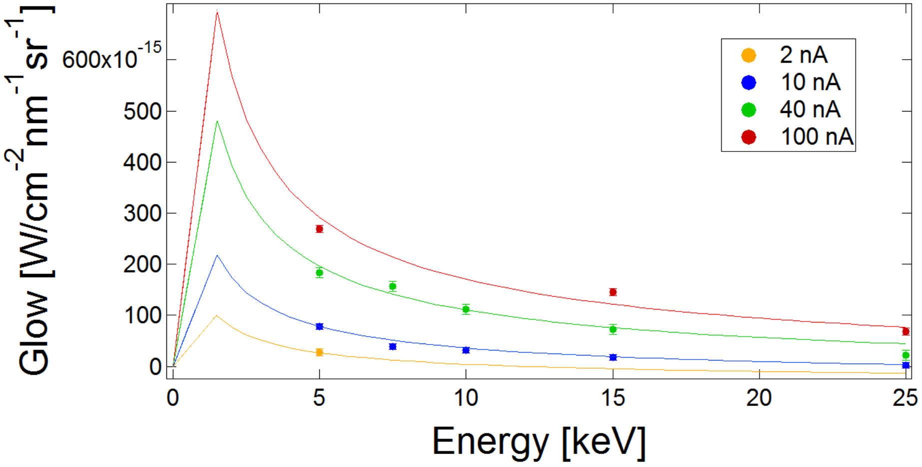


Cathodoluminescence—E_b and Range Dependence

Incident Beam Energy

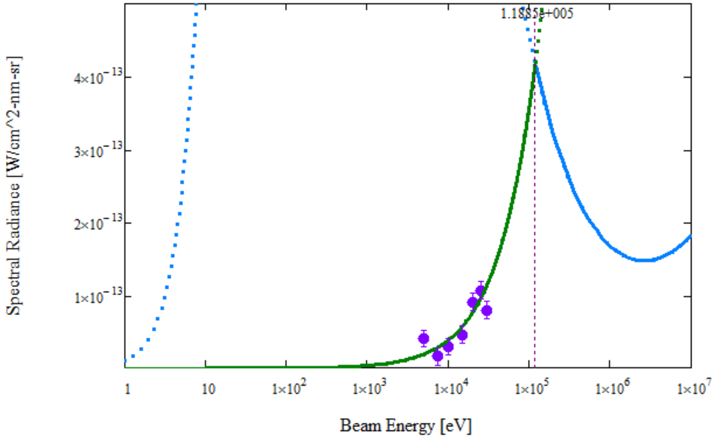
$$\dot{D}(J_b, E_b) = \frac{\boxed{E_b}\, J_b[1-\eta(\boxed{E_b})]}{q_e \rho_m} \times \begin{cases} [1/L] & ; R(E_b) < L \\ [1/R(\boxed{E_b})] & ; R(E_b) > L \end{cases}$$



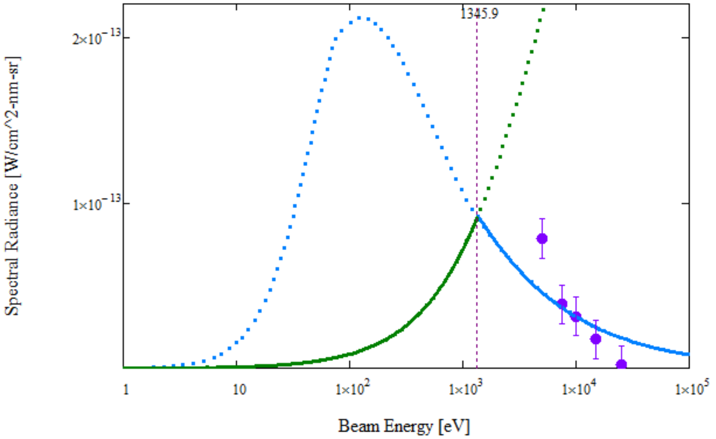
Nonpenetrating Radiation {$R(E_b) < L$}: all incident power absorbed in coating and intensity and dose rate are linear with incident power density

Penetrating Radiation {$R(E_b) > L$}: absorbed power reduced by factor of $L/R(E_b)$.

Nonpenetrating: Low E_b, Thick



Penetrating: High E_b, Thin



Can map $R(E_b)$ with inflection points

Cathodoluminescence—J_b and Dose Dependence

Cathodoluminescence intensity (α emitted power)

$$I_\gamma(J_b,E_b,T,\lambda) \propto \frac{\dot{D}(\boxed{J_b},E_b)}{\dot{D}+\dot{D}_{sat}}\left\{\left[1-e^{-(\varepsilon_{ST}/k_BT)}\right]\right\}$$

Dose rate (α adsorbed power)

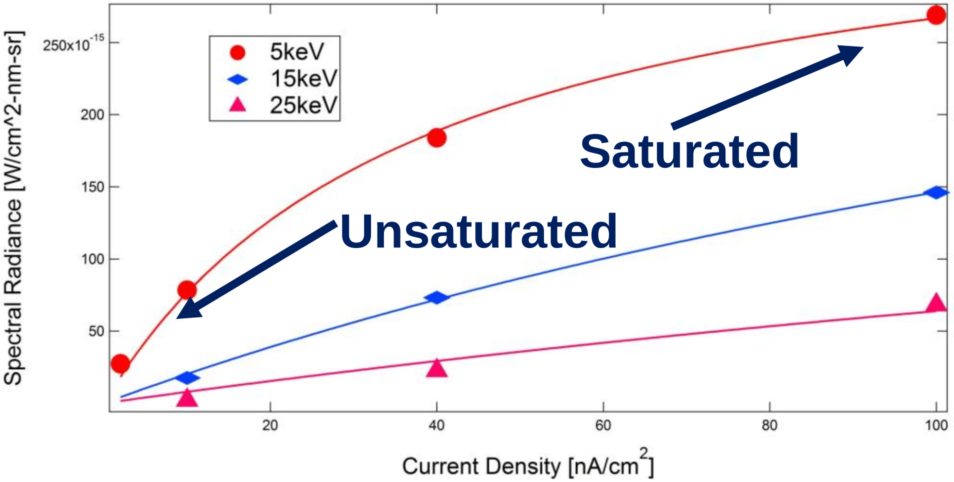
$$\dot{D}(J_b,E_b) = \frac{E_b\boxed{J_b}[1-\eta(E_b)]}{q_e\rho_m} \times \begin{cases}[1/L] & ;\ R(E_b)<L \\ [1/R(E_b)] & ;\ R(E_b)>L\end{cases}$$

$\dot{\mathrm{D}}_{sat}$

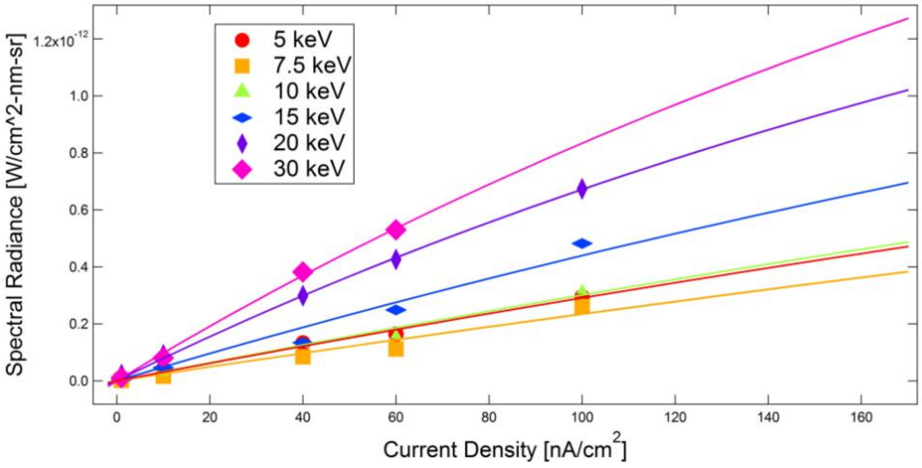
~10 Gy/s for SiO_2 coatings.

Measure of charge required to fill traps.

Nonpenetrating: Low E_b, Thick



Penetrating: High E_b, Thin



Cathodoluminescence—T Dependence

Cathodoluminescence intensity (α emitted power)

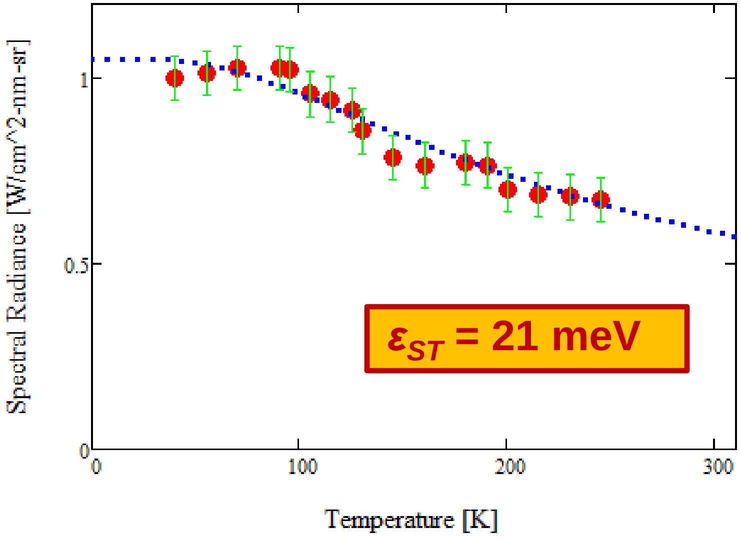
$$I_\gamma(J_b, E_b, T, \lambda) \propto \frac{\dot{D}(J_b, E_b)}{\dot{D} + \dot{D}_{sat}} \{[1 - e^{-(\varepsilon_{ST}/k_B T}]\}$$

Thermal dependence of luminescence proportional to:

Characterized by energy depth of shallow traps below the conduction band, ε_{ST}

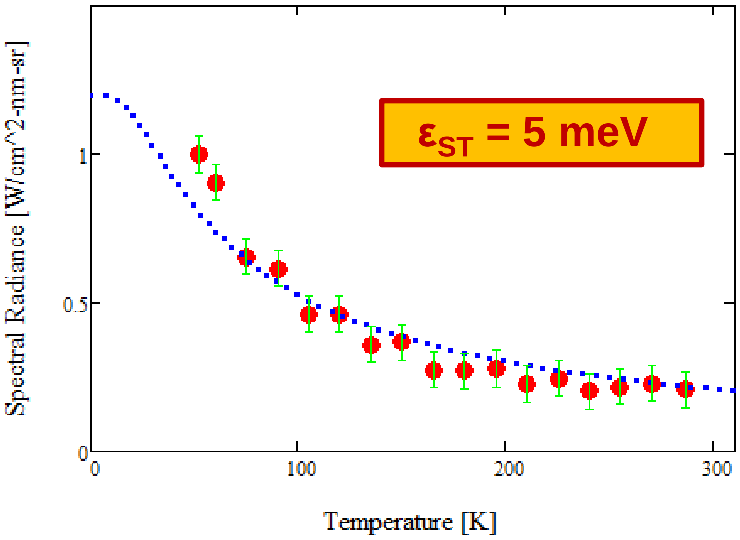
Proportional to fraction of electrons retained in shallow traps and not thermally excited into CB

Highly disordered sputtered deposited
60 nm thin sample



ε_{ST} = 21 meV

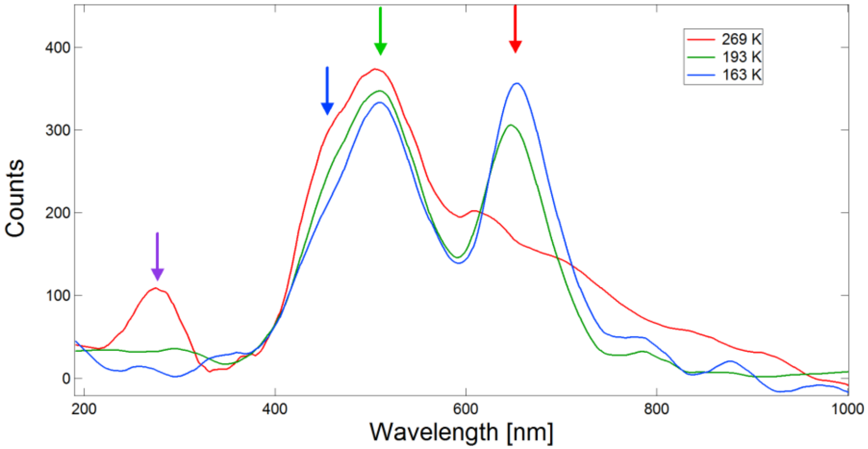
Disordered hydrolysis formed SiO_2
80 μm thick sample

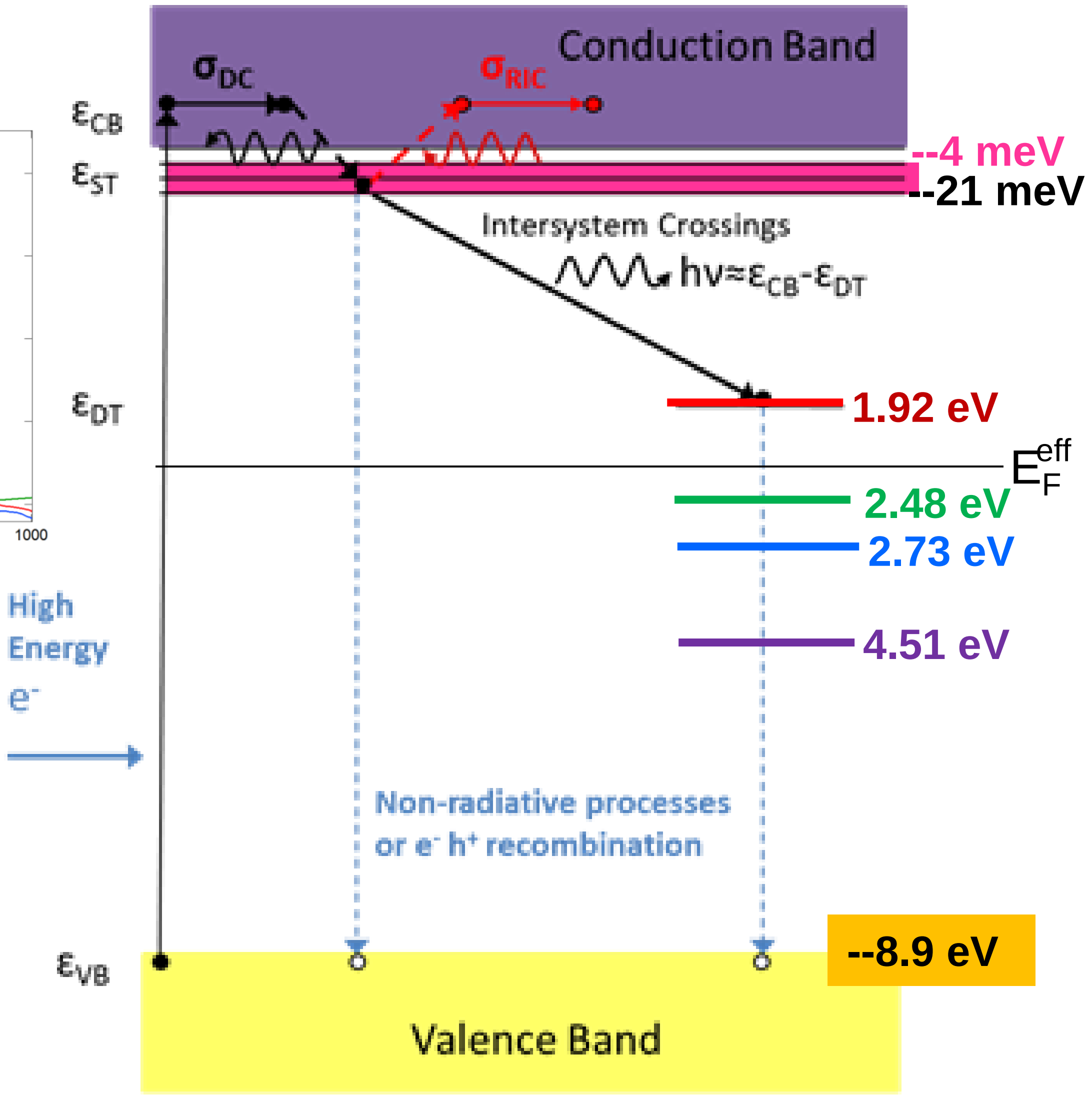


ε_{ST} = 5 meV

Cathodoluminescence Emission Spectra

Photon Emission Spectra Peak Wavelength

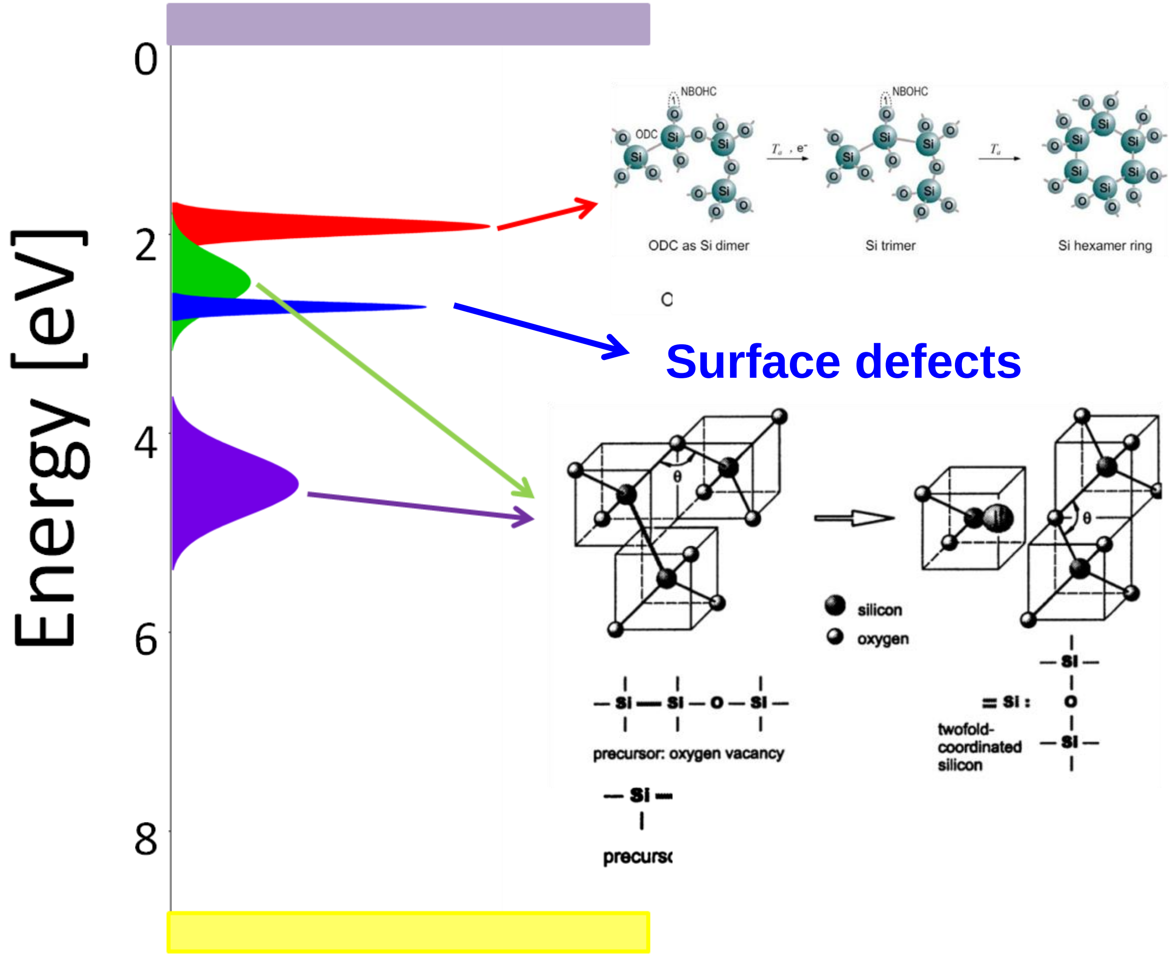




Multiple peaks in spectra correspond to multiple DOS distributions

Peak positions ←→ Center of DOS
Peak amplitude ←→ N_T
Peak width ←→ DOS width

Cathodoluminescence—Defect Origins for DOS’s



Surface defects

Based on peak positions for similar disordered SiO_2 samples at room temperature.

Sahl identified 1.98 eV peak as from nonbridging oxygen hole center.

Trukhin identified 2.48 eV and 4.51 eV peaks as from an oxygen deficient center.

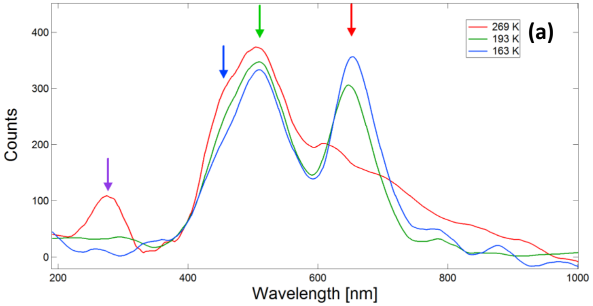
Mitchell identified 2.75 eV peak with surface defects

The long lifetimes of the DT states produce Gaussian shaped spectral bands.

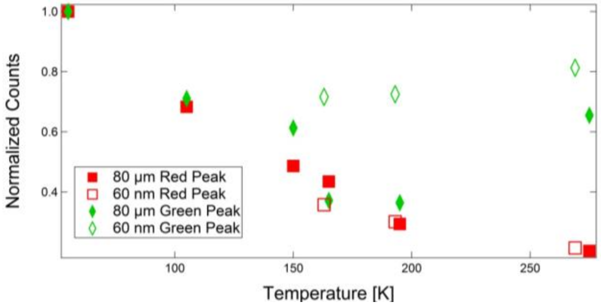
Occupation of DOS's from Emission Spectra

Information on effective Fermi level and DOS occupation

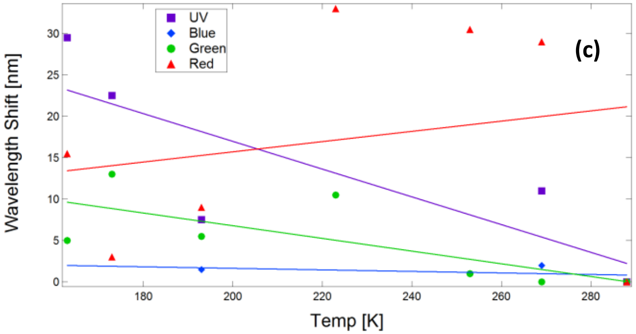
Width vs T

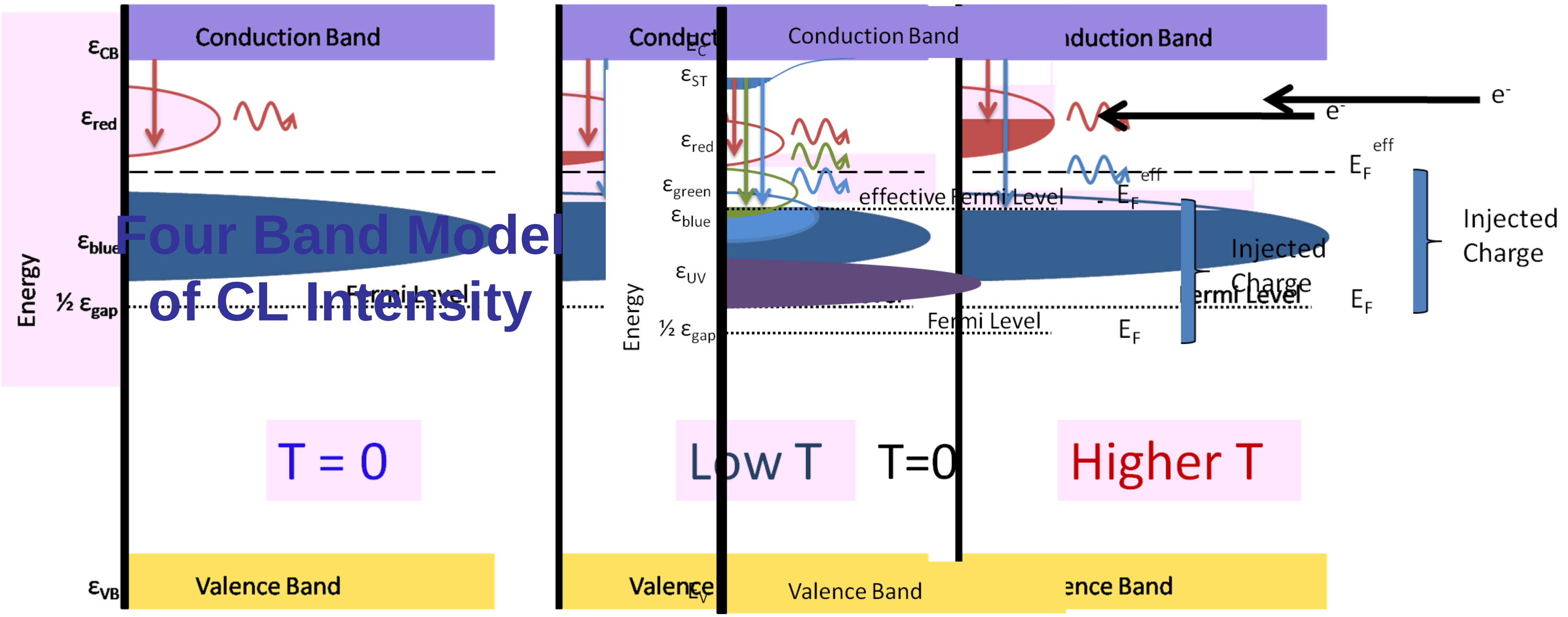


Peak Intensity vs T



Wavelength shift vs T





Four Band Model of CL Intensity

Conclusions--Total Intensity Model

$$I_\gamma(J_b,E_b,T,\lambda) \propto \frac{\dot{D}(J_b,E_b)}{\dot{D}+\dot{D}_{sat}}\{[1-e^{-(\varepsilon_{ST}/k_B T)}]\}\{[1-\mathbb{A}_f(\lambda)][1+\mathbb{R}_m(\lambda)]\}$$

$$\dot{D}(J_b,E_b) = \frac{E_b J_b[1-\eta(E_b)]}{q_e \rho_m} \times \begin{cases} [1/L] & ;\ R(E_b) < L \\ [1/R(E_b)] & ;\ R(E_b) > L \end{cases}$$

- **CL was observed for disordered SiO_2 under incident electron irradiation**
- **This work validated the proposed model for intensity dependence on**
  - **Beam Current Density**
  - **Beam Energy**
  - **Material Temperature**
- **Overall intensity has not been modeled previously**

Conclusions--DOS

- Validated proposed four band model.

Starting with the observation of cathodoluminescence

- 4 spectral bands present produced by the CL.
- Temperature-dependent behavior of these bands from 280 K to 50 K follow the prediction.
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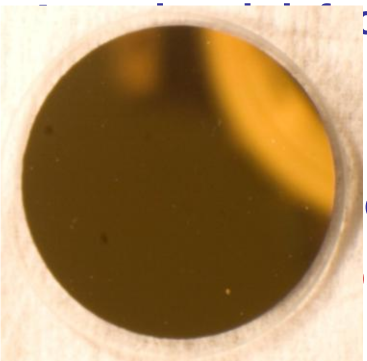

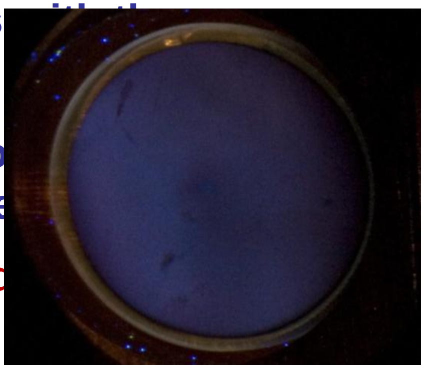

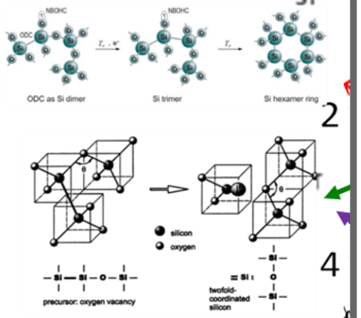

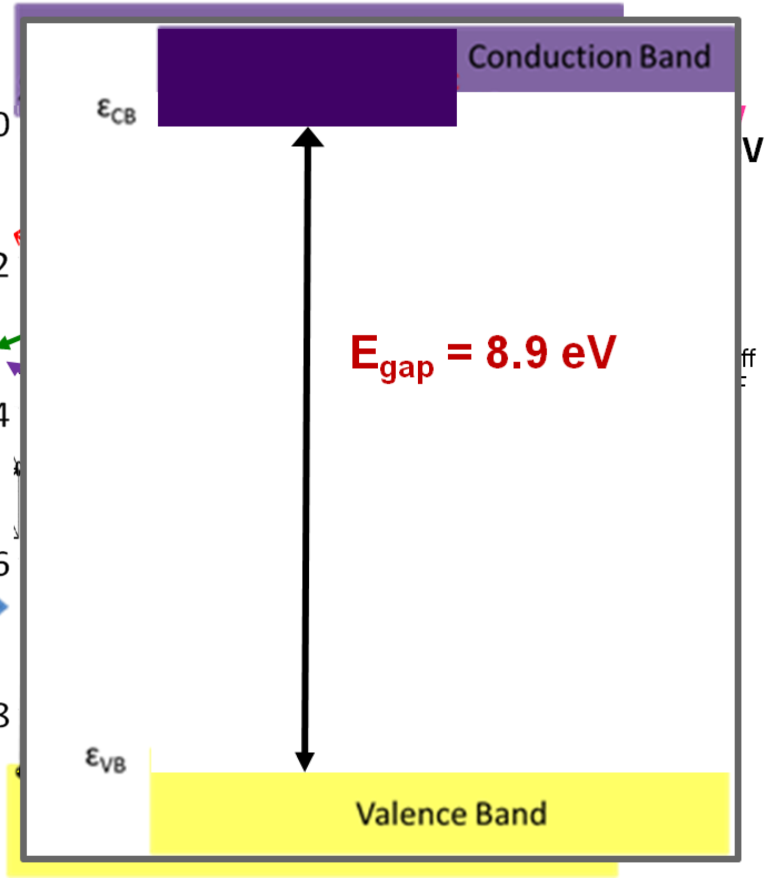

  - Deep trap bands, defect origins, energies, shapes and occupancies
  - Effective Fermi level dependence with T and Ḋ

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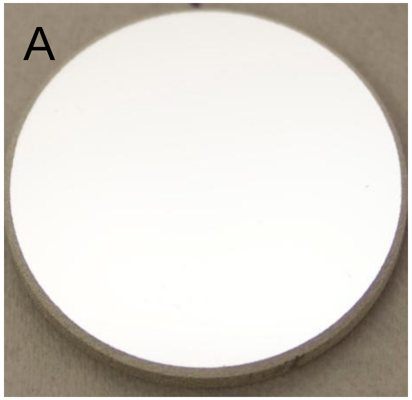
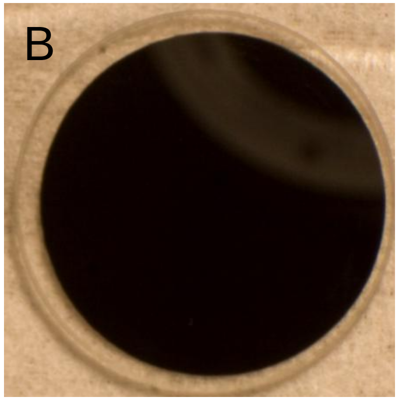
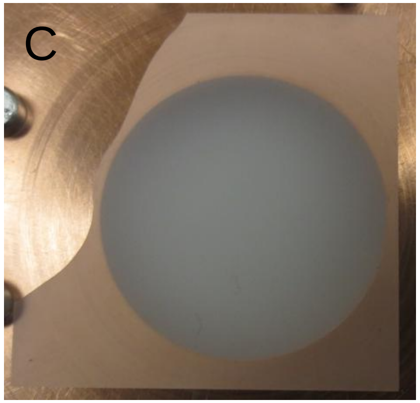
Supplemental Slides

Samples

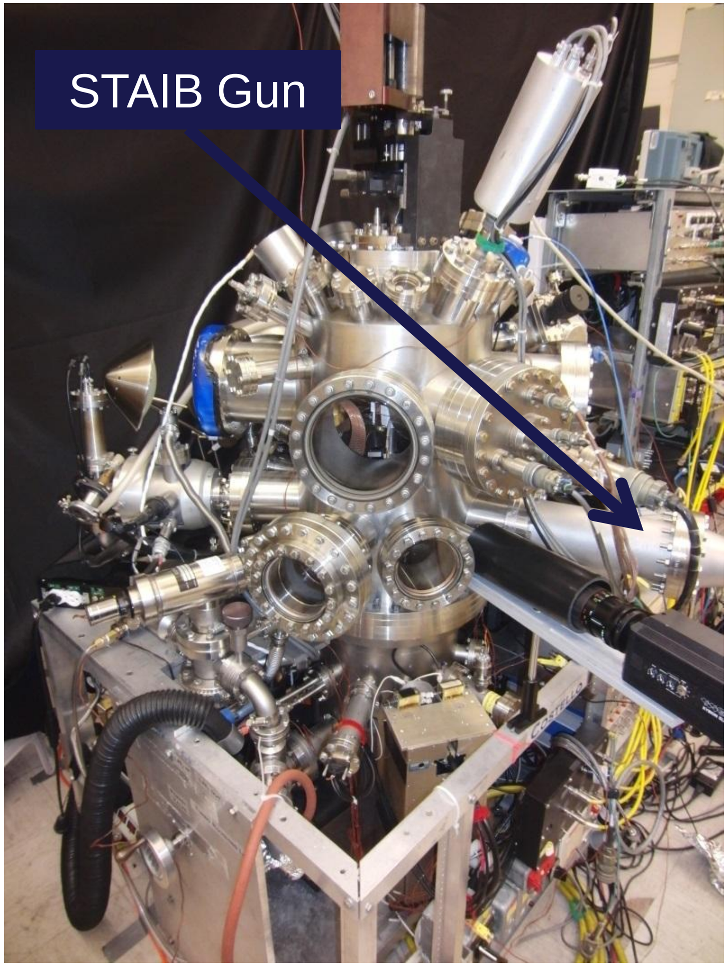
Experiment	Sample	Thickness	Electron Source	Sample Holder	Luminescent Data Collected
A	POM	~60 nm	Kimball (5-30 keV)	Carousel	J_b, E_b dependent
B	Primary Mirror	~60 nm	STAIB (200 eV- 5 keV)	Carousel	T dependent
C	Bulk Sample	~80 µm	Kimball (5-30 keV)	Sample Round	J_b, E_b, T dependent



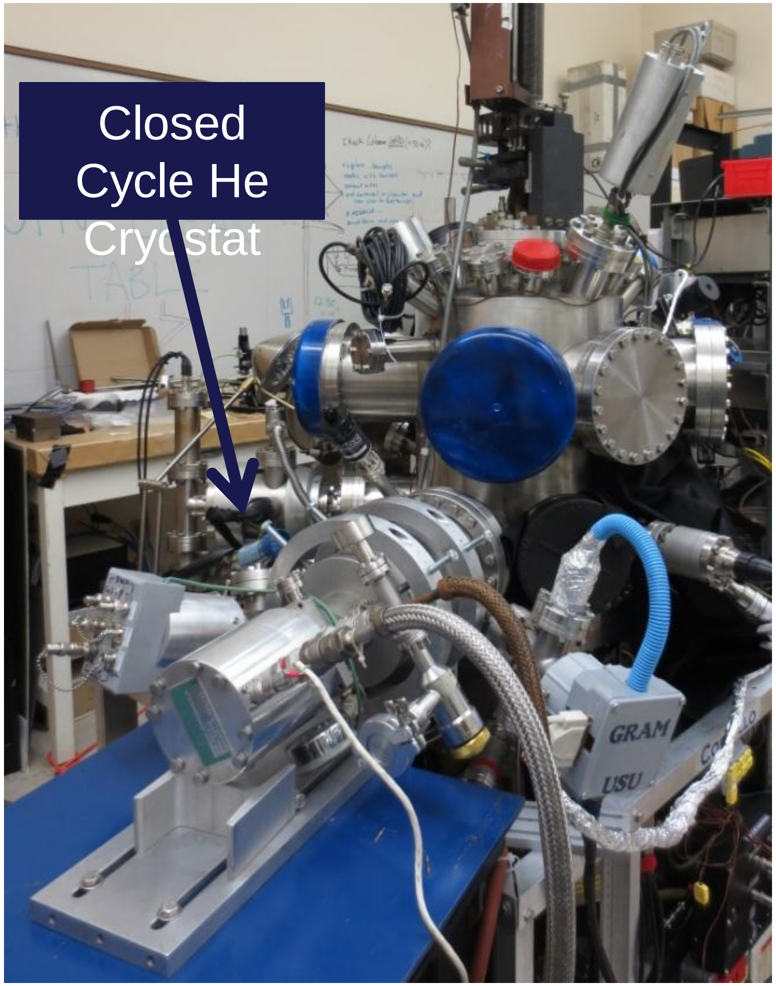




Instrumentation

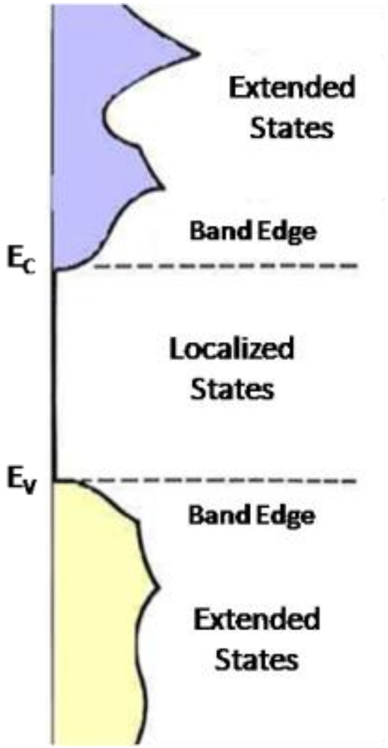


STAIB Gun

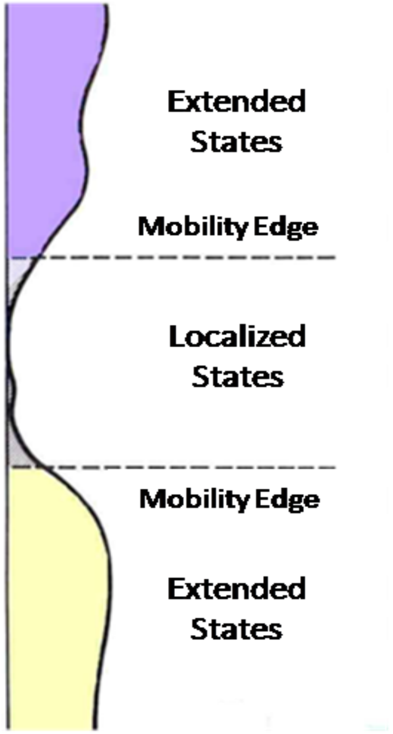


Closed Cycle He Cryostat

Electron Band Model of Ordered vs Disordered Materials



transition from ordered to disordered materials



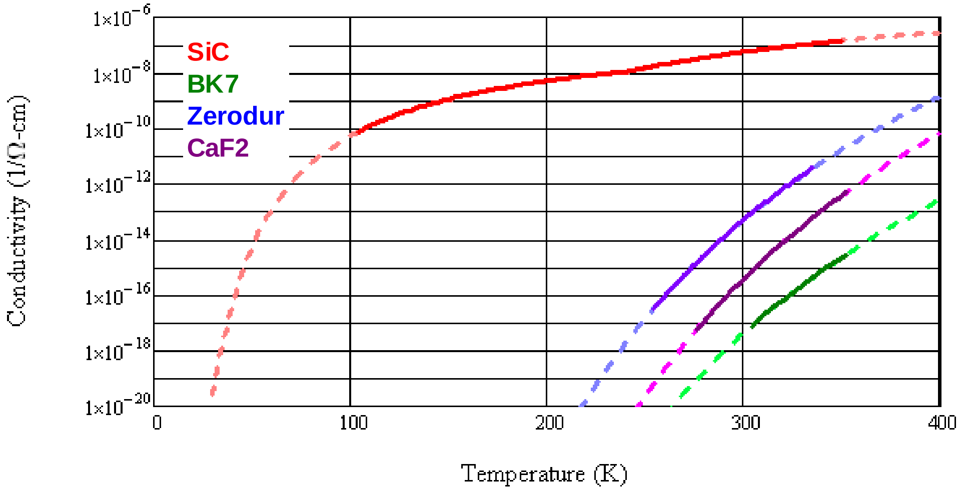
Crystalline SiO_2

•band gap is empty; no localized states in an ordered material between the VB edge (E_V) and the CB edge (E_C).

Disordered SiO_2

- with disorder, trap states begin to occupy the band gap.
- trap states of fused silica consist of ST and DT states.
- ST states are located within K_bT of E_C, and are created by minor, low energy, defects.
- DT states are located >K_bT of E_C, created by more drastic, high energy defects.

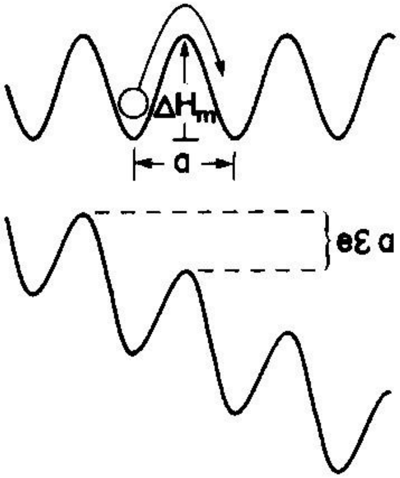
Conductivity vs Temperature

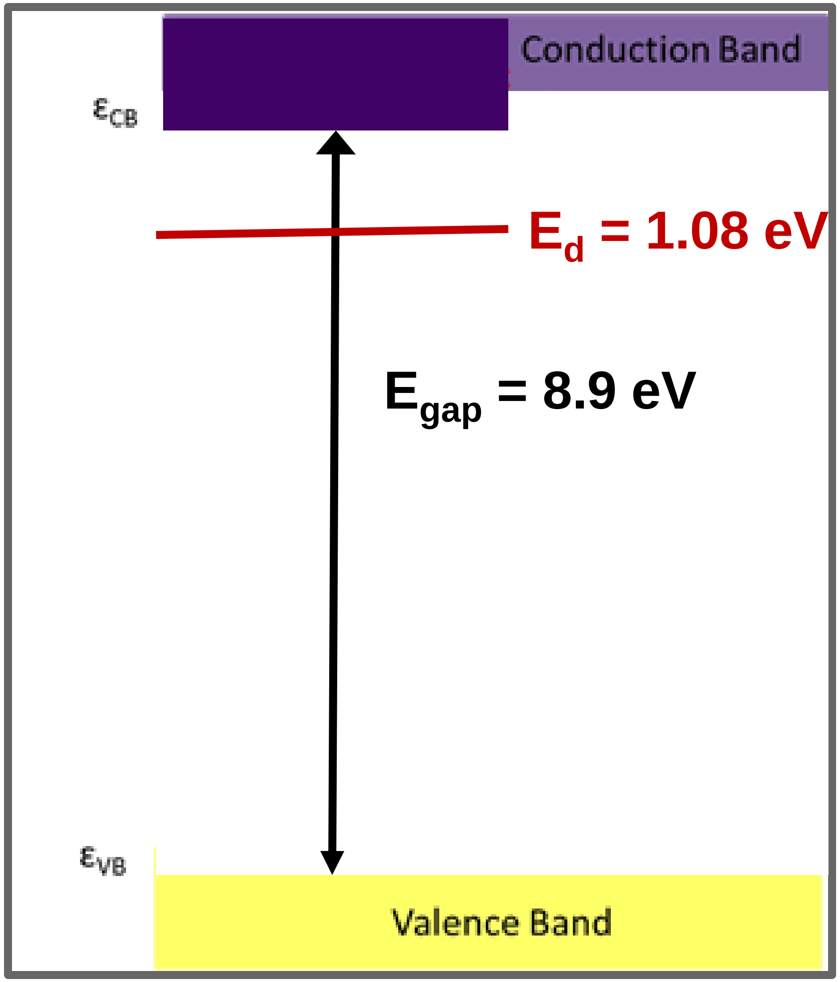


$$\sigma_{hop}(E,T)=\left[\frac{2\cdot n(T)\cdot \nu\cdot a\quad\cdot e}{E}\right]\exp\left[\frac{-\Delta H}{k_B\cdot T}\right]\sinh\left[\frac{\varepsilon\cdot E\cdot a}{2\cdot k_B\cdot T}\right]$$

Yields:

Defect energy, E_d and Trap density, N_T





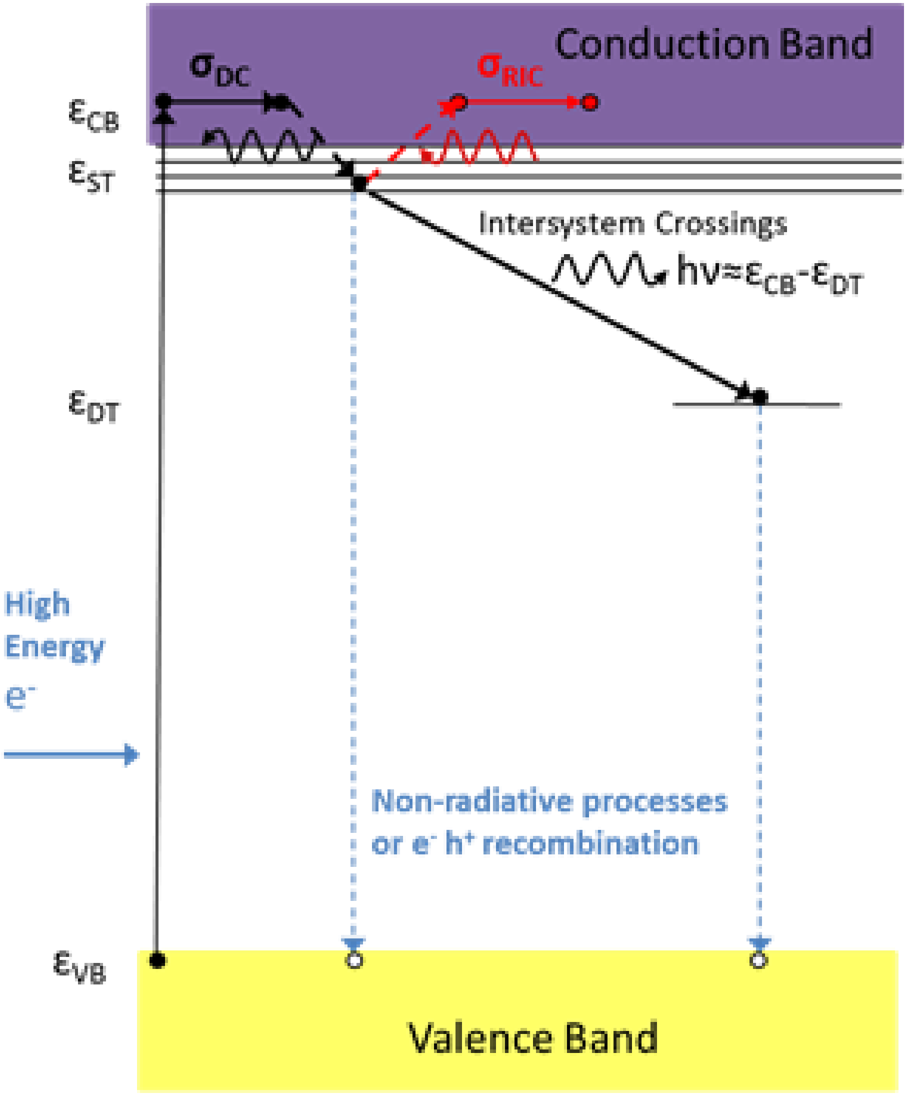
Complementary Responses to Radiation

Modified Joblonski band diagram

- VB electrons excited into CB by the high energy incident electron radiation.
- They relax into shallow trap (ST) states, then thermalize into lower available long-lived ST.

- **Four paths are possible:**

(i) Remain in (short lived) shallow traps
(ii) relaxation to deep traps (DT), with concomitant photon emission;
(iii) radiation induced conductivity (RIC), with thermal re-excitation into the CB; or
(iv) non-radiative transitions or e^--h^+ recombination into VB holes.



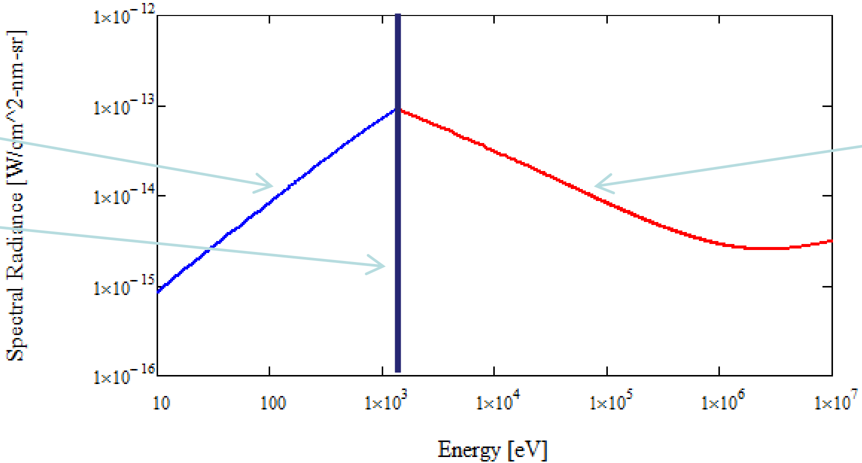
Single (Mean) Band Model of CL Intensity

Below Saturation Dose Rate

Incident Beam Energy

$$I_\gamma(J_b,E_b,T,\lambda) \propto \frac{\dot{D}(J_b,E_b)}{\dot{D}+\dot{D}_{sat}}\{[1-e^{-(\varepsilon_{ST}/k_BT)}]\}\{[1-\mathbb{A}_f(\lambda)][1+\mathbb{R}_m(\lambda)]\}$$

$$\dot{D}(J_b,E_b) = \frac{E_b\,J_b[1-\eta(E_b)]}{q_e\rho_m}\times\begin{cases}[1/L] & ;\ R(E_b)<L\\ [1/R(E_b)] & ;\ R(E_b)>L\end{cases}$$



nonpenetrating

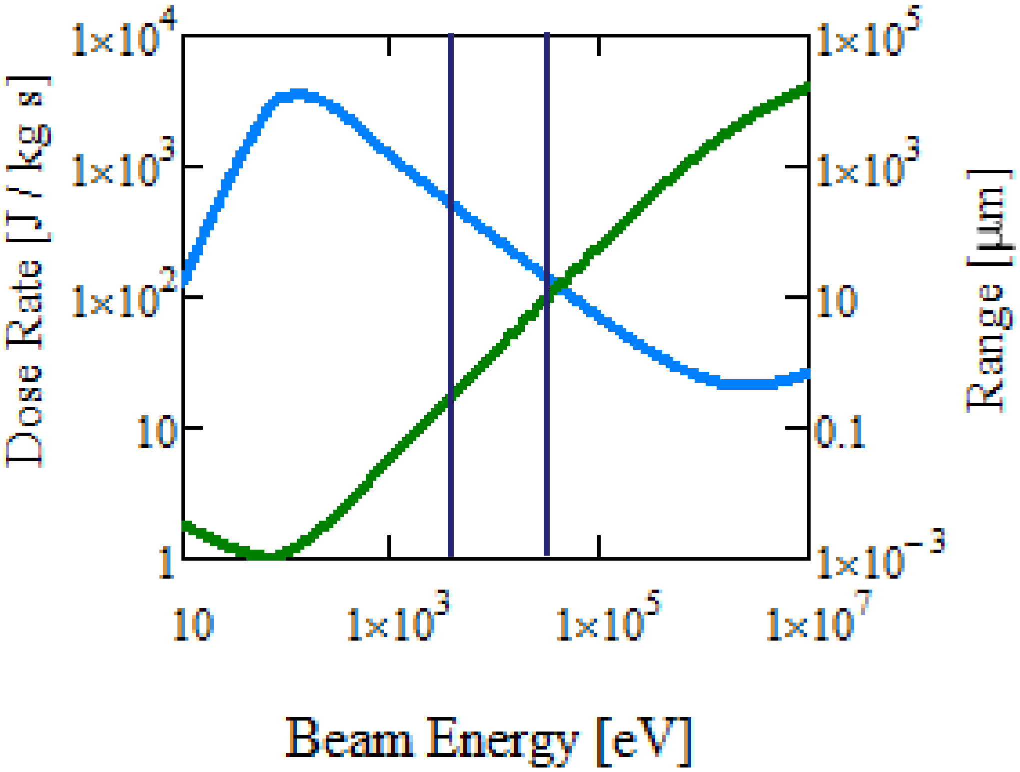
penetrating

penetration energy (1.3 keV)

- CL intensity depends on dose rate through the energy-dependent range of the beam within the material.
- When the incident beam is nonpenetrating, the CL intensity increases linearly as the beam energy increases; all power in the beam is deposited in the material.
- Increasing energy increases number of VB electrons excited to the CB which then contribute to CL.
- At the penetration energy, the range exceeds material thickness and beam becomes penetrating.
- Some of the incident beam power is lost, or not deposited in the material and intensity begins to fall off with increasing energy.

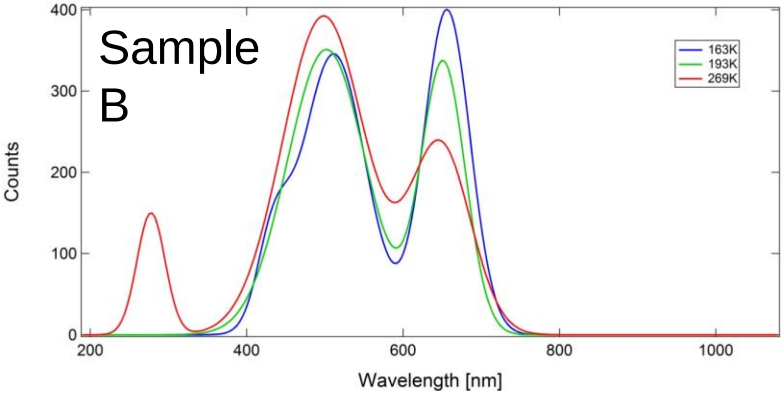
Single (Mean) Band Model of CL Intensity

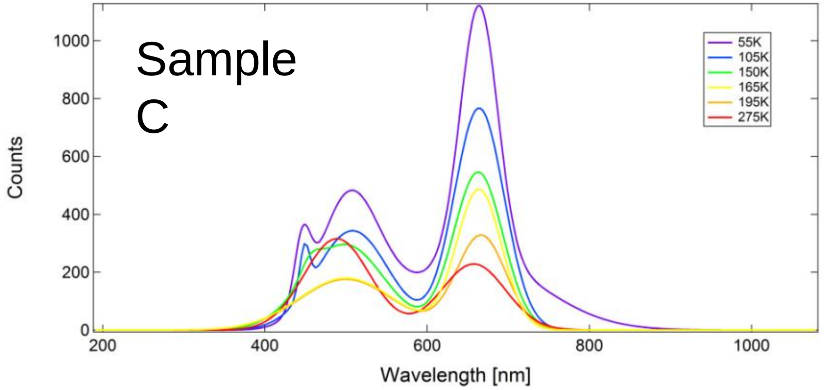
Dose Rate and Range



Range (green) and dose rate (blue) of disordered SiO_2 as a function of incident energy using the continuous slow-down approximation, based on calculations from (Wilson and Dennison, 2012).

4 Band Model--Details





- two different materials produced spectra which were similar in the peaks observed, but not entirely the same in terms of relative peak intensity; the defect density of states varies from one fused silica sample type to the next.
- the data were acquired for Sample B from 280 K to 160 K and for Sample C from 280 K to 50 K, so the behavior of the two samples cannot be compared below 160 K.
- raw spectral data were fit with composite curves with four Gaussian functions (instrumentation has been ruled out since the resolution of the spectrometer, 0.5 nm, << width of the bands, ~20-50 nm, depending on the band, indicating the long lifetimes of the DT defect states).
- spectra for Sample B and Sample C had two dominant bands centered at ~500 nm and ~645 nm; an additional shoulder was observed at ~455 nm at low temperature. A fourth peak in the UV range at ~275 nm was observed for the thin Sample B; the UV range below ~350 nm, was not measured for the thick Sample C.
- the four peaks in the disordered SiO_2 luminescence spectra are attributed to bands of localized defect or DT states, at ~1.93, ~2.48, ~2.76, and ~4.97 eV below the ST.