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Cathodoluminescence Studies of the Density of States of Disordered Silicon Dioxide

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Cathodoluminescence Studies of the Density of States of Disordered Silicon Dioxide

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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 $\sim 8.9$ eV
- Additional steps in transmission in 1-4 eV range
Cathodoluminescence—Deep and Shallow Trap DOS

Cathodoluminescence intensity ($\alpha$ emitted power)

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

Dose rate ($\alpha$ adsorbed power)

\[
\dot{D}(J_b, E_b) = \frac{E_b J_b [1 - \eta(E_b)]}{q_e \rho_m} \times \left\{ \begin{array}{ll}
\frac{1}{L} & ; R(E_b) < L \\
\frac{1}{R(E_b)} & ; R(E_b) > L
\end{array} \right.
\]

- $J_b$: incident current density
- $E_b$: incident beam energy
- $T$: temperature
- $\lambda$: photon wavelength
- $q_e$: electron charge
- $\rho_m$: mass density
- $L$: Sample thickness
- $\varepsilon_{ST}$: shallow trap energy
- $\eta(E_b)$: backscatter yield
- $\dot{D}$: saturation dose rate
- $R(E_b)$: penetration range

The diagram illustrates the energy levels in the conduction band and valence band, with transitions involving non-radiative processes and intersystem crossings.

The equation on the left describes the cathodoluminescence intensity as a function of the incident beam energy, temperature, and photon wavelength, taking into account the backscatter yield and penetration range.
Cathodoluminescence—$E_b$ and Range Dependence

Incident Beam Energy

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

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 ($\alpha$ emitted power)

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

Dose rate ($\alpha$ adsorbed power)

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

Nonpenetrating: Low $E_b$, Thick

Penetrating: High $E_b$, Thin

$\dot{D}_{sat} \approx 10 \text{ Gy/s for SiO}_2 \text{ coatings.}$

Measure of charge required to fill traps.
Cathodoluminescence—T Dependence

Cathodoluminescence intensity ($\alpha$ emitted power)

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

Thermal dependence of luminescence proportional to:

Characterized by energy depth of shallow traps below the conduction band, $\varepsilon_{ST}$

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

Highly disordered sputtered deposited 60 nm thin sample

Disordered hydrolysis formed SiO$_2$ 80 µm thick sample

\( \varepsilon_{ST} = 21 \text{ meV} \)

\( \varepsilon_{ST} = 5 \text{ meV} \)
**Cathodoluminescence Emission Spectra**

**Photon Emission Spectra**

**Peak Wavelength**

- 1.92 eV
- 2.48 eV
- 2.73 eV
- 4.51 eV
- 8.9 eV

**Count**

- 269 K
- 193 K
- 163 K

**Wavelength [nm]**

- 200
- 400
- 600
- 800
- 1000

**Multiple peaks in spectra correspond to multiple DOS distributions**

- Peak positions ↔ Center of DOS
- Peak amplitude ↔ N_T
- Peak width ↔ DOS width

**Peak positions**

- Center of DOS
- Non-radiative processes or e^- h^+ recombination

**Valence Band**

**Conduction Band**

**Eff**

- 1.92 eV
- 2.48 eV
- 2.73 eV
- 4.51 eV

**Eff**

- -4 meV
- -21 meV

**Intersystem Crossings**

- hν = ε_CB - ε_DT
Cathodoluminescence—Defect Origins for DOS’s

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

Conduction Band

Valence Band

\( \epsilon_{CB} \)

\( \epsilon_{VBA} \)

\( \epsilon_{red} \)

\( \epsilon_{blue} \)

\( \frac{1}{2} \epsilon_{gap} \)

\( \epsilon_{green} \)

\( \epsilon_{UV} \)

\( \epsilon_{ST} \)

\( E_F \)

\( E_{F,\text{eff}} \)

\( e^- \)

\( \text{Injected Charge} \)

\( T = 0 \)

Low T

\( T = 0 \)

Higher T

Energy
\[ I(\gamma, J_b, E_b, T, \lambda) \propto \frac{\dot{D}(J_b, E_b)}{\dot{D} + \dot{D}_{sat}} \left[ 1 - e^{-\left(\frac{\varepsilon_{ST}}{k_B T}\right)} \right] \left[ 1 - A_f(\lambda) \right] \left[ 1 + R_m(\lambda) \right] \]

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

- CL was observed for disordered SiO\textsubscript{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.
- 4 spectral bands present produced by the CL.
- Temperature-dependent behavior of these bands from 280 K to 50 K follow the prediction.
- Associated defects with the bands.
- Developed more complete picture of disordered DOS
  - Shallow traps density and occupancies
  - Deep trap bands, defect origins, energies, shapes and occupancies
  - Effective Fermi level dependence with T and $\dot{D}$

Starting with the observation of cathodoluminescence
## Samples

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>Thickness</th>
<th>Electron Source</th>
<th>Sample Holder</th>
<th>Luminescent Data Collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>POM</td>
<td>~60 nm</td>
<td>Kimball (5-30 keV)</td>
<td>Carousel</td>
<td>$J_b$, $E_b$ dependent</td>
</tr>
<tr>
<td>B</td>
<td>Primary Mirror</td>
<td>~60 nm</td>
<td>STAIB (200 eV- 5 keV)</td>
<td>Carousel</td>
<td>T dependent</td>
</tr>
<tr>
<td>C</td>
<td>Bulk Sample</td>
<td>~80 µm</td>
<td>Kimball (5-30 keV)</td>
<td>Sample Round</td>
<td>$J_b$, $E_b$, T dependent</td>
</tr>
</tbody>
</table>
Instrumentation

STAIB Gun

Closed Cycle He Cryostat
Electron Band Model of Ordered vs Disordered Materials

transition from ordered to disordered materials

Crystalline SiO₂
• band gap is empty; no localized states in an ordered material between the VB edge ($E_V$) and the CB edge ($E_C$).

Disordered SiO₂
• 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 $K_b T$ of $E_C$, and are created by minor, low energy, defects.
• DT states are located $> K_b T$ of $E_C$, created by more drastic, high energy defects.
Conductivity vs Temperature

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

Yields:

- Defect energy, \( E_d \)
- Trap density, \( N_T \)

\( E_d = 1.08 \text{ eV} \)

\( E_{\text{gap}} = 8.9 \text{ eV} \)

\( \varepsilon_{CB} \) and \( \varepsilon_{VB} \)
**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:
  1. Remain in (short lived) shallow traps
  2. Relaxation to deep traps (DT), with concomitant photon emission;
  3. Radiation induced conductivity (RIC), with thermal re-excitation into the CB; or
  4. Non-radiative transitions or e⁻-h⁺ recombination into VB holes.
• 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).
• 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, $\sim$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 $\sim$500 nm and $\sim$645 nm; an additional shoulder was observed at $\sim$455 nm at low temperature. A fourth peak in the UV range at $\sim$275 nm was observed for the thin Sample B; the UV range below $\sim$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 $\sim$1.93, $\sim$2.48, $\sim$2.76, and $\sim$4.97 eV below the ST.