Topics in Evanescent Wave Cavity Ring-down Spectroscopy (EW-CRDS)

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Topics in Evanescent Wave Cavity Ring-down Spectroscopy (EW-CRDS)

Outline

1. EW-CRDS preliminaries
2. Monolithic Optical Resonators for EW-CRDS
   a. Total-internal-reflection (TIR)-ring resonator
   b. Monolithic folded resonator
3. Recent results on H-atom interactions in a-Si
   Relevant to a-Si solar cells (Staebler-Wronski effect)
Motivation

To extend CRDS to thin films, interfaces, nano-materials

> Use evanescent waves – ideally suited probe

> Maintain sensitivity compared to gas-phase CRDS

> Permit polarization-dependent measurements

To enable unique measurements - otherwise unachievable.
Evanescent waves: Properties & Advantages

R=1 in principle for TIR for $\Theta_i > \Theta_c$

In practice, limited by surface scattering.

$R \approx 0.999999$ for RMS roughness $\sim 0.05$ nm in the visible.

Broad bandwidth ($n_1$ changes slowly with wavelength).

**Surface selective:**

- Locally enhanced surface E-field
- Surface E-field direction easily controlled
- E-field components in all directions: $(x, y, z)$
- Nano-length scale ($d_p \sim \lambda$): Reduces bulk signal
Early EW-CRDS Prototype

\[ \tau = \frac{t_r}{L_{\text{mirrors}} + L_{\text{bulk}} + L_{\text{surf}} + L_{\text{pol}} + L_{\text{ads}}} \]

Adsorbed I$_2$ detection limit $\sim$4% of a monolayer estimated

Only P-polarization is resonant; S-information is lost

Large losses for P-polarization: Total loss >5000 ppm!
Monolithic Resonators

1. Eliminate intra-cavity interfaces.
2. Small size $\sim 1$-$3$ cm$^3$ for small bulk loss.
3. Relatively easy to use in-situ.

Choose optimal design:
Broadband, narrowband, or multi-region

Choose $\Theta_i$: Thin films or Liquids
Minimize Loss - Maximize Sensitivity

Cost $\sim$ A few flashlamp replacements ($\sim$2K Euros/optic)
Monolithic TIR-ring Resonator

All TIR gives broad bandwidth.
Convex facet imparts stability.
Input/Output coupling by photon tunneling.

Material - selected fused silica: Loss \( \sim 200 \text{ ppm/cm} \) at 450 nm
\( 50 \text{ ppm/cm} \) at 550 nm
\( 7 \text{ ppm/cm} \) at 1400 nm
\( 3 \text{ ppm/cm} \) at 1200 nm & 1600 nm
\( 1 \text{ ppm/cm} \) at 1550 nm
TIR-ring resonator: Experimental details

S and P measured simultaneously
Extinction Ratio $\sim 10^{-5}$
Molecular Orientation Measurement

Before I₂ adsorption

After I₂ adsorption

Large difference in Loss for S- vs P-polarization.

E-field: $I_z \sim 7$ (normal to surface)   $I_y \sim 4$ and $I_x \sim 0.2$ (in-plane)

Results indicate I₂ molecules lay flat on average.
Overtones of adsorbed HNO$_3$

> 2vOH and 3vOH regions for HNO$_3$ adsorbed on SiO$_2$
> Demonstrates $\sim 1000$ cm$^{-1}$ of bandwidth in the near IR.
> Tunneling gap-width held constant.
> A predominance of HNO$_3$:H$_2$O complex is observed.
Evaluating the Detection Limit for EW-CRDS

$$\text{MDA} = L_0(\Delta \tau/\tau) = \Gamma_y N_s \sigma_s(\omega) \sec(\theta_i)$$

$$\Gamma_y = \text{effective field enhancement (Need } \Theta_{\text{avg}})$$

$$\sigma_s(\omega) = \text{surface cross section}$$

$$N_s = \text{surface density}$$

$$\theta_i = \text{angle of incidence}$$

$$\left( N_s \right)_{\text{min}} \quad \left( \text{Coverage} \right)_{\text{min}}$$

I$_2$: $\sigma_s(\omega) \sim 10^{-18} \text{ cm}^2 \Rightarrow N_s \sim 10^{10}/\text{cm}^2 \text{ or } 60 \text{ ppm ML}$

Dye: $\sigma_s(\omega) \sim 10^{-16} \text{ cm}^2 \Rightarrow N_s \sim 10^8/\text{cm}^2 \text{ or } <1 \text{ ppm ML}$

3vOH: $\sigma_s(\omega) \sim 10^{-22} \text{ cm}^2 \Rightarrow N_s \sim 10^{13}/\text{cm}^2 \text{ or } 1% \text{ ML}$
Monolithic Folded Resonator

Sample area at apex: 85x99 µm

Center Wavelength = 1205 nm
Base loss = 18 ppm/pass (coating limited)
Bulk loss < 5 ppm (L/2 = 2 cm)
MDA = 3x10^{-8} 5.3 µs ring-down time
Applications of the Folded Resonator

1. Spectroscopy of the intrinsic surface OH groups and H$_2$O adlayer.

2. Absolute surface coverage measurement using the C-H stretching overtone.

3. Kinetics of “dangling bond” defect creation and healing in a-Si.
Spectroscopy of Atomically Smooth SiO₂

Left: $2\nu\text{OH} + \delta\text{OH}$ modes of SiOH

Right: $2\nu\text{OH} + \delta\text{OH}$ modes of adsorbed H₂O

> Highly polarized and relatively sharp features

> Black plots: Under dry N₂ for several weeks.

> Grey plots: Under 10% Relative Humidity

A three-quantum process: 2 stretching quanta + 1 quantum bending excitation
The $\text{H}_2\text{O}$ peaks saturate…

Baseline corrected data for different relative humidity (RH) levels.

SiOH peaks (2) are close to literature values; SiOH peaks are oppositely polarized.

Three $\text{H}_2\text{O}$ peaks out of 4 show saturation with increasing RH:

First monolayer is distinct.
The H$_2$O lines also sharpen...

**H$_2$O**

- FWHM: 11.3 cm$^{-1}$ $\rightarrow$ 10.4 cm$^{-1}$
- Area: 61% increase

**SiOH**

- FWHM: 10.2 cm$^{-1}$ $\rightarrow$ 11.5 cm$^{-1}$
- Area: 15% decrease

- H$_2$O peaks sharpen; SiOH peaks broaden
- Increased ordering seems a likely explanation
Interpretation: A quasi-ice layer

SiO₂ surface is quasi-crystalline:
1. SiOH peaks are highly polarized
2. SiOH peaks are relatively sharp
3. Related observations in the literature
4. Consistent with (100) facet of cristobalite
   (Two peaks; oppositely polarized)

H₂O layer H-bonds to SiOH forming a quasi-ice layer:
1. H₂O peaks are highly polarized.
2. H₂O peaks are relatively sharp.
3. H₂O peaks saturate as a function of RH.
4. H₂O peaks sharpen at a full monolayer.

Geminal hydroxyls

“Ice Tessellation”
From Yang et al. PRL 92(14), 2004

>ALSO - SiOH groups show similar thermal stability to OH groups on Al(0001)

Role of dipolar coupling?
Absolute Coverage Measurement

Why measure absolute coverage?

1. Fundamental to surface science
2. Absolute surface reaction rate constants
3. For understanding sensor response

Procedure for absolute coverage measurement:

1. Measure absolute (integrated) intensity in a reference state.
2. From EW-CRDS spectra, obtain average orientation.
3. Use conservation of the integrated intensity:

\[ N_s = \frac{2 \cos \theta_i \int L_{\text{abs,TE}}(\omega) \, \omega^{-1} d\omega}{3 I_y \sin^2(\Theta_{\text{avg}}) \int \sigma_0(\omega) \, \omega^{-1} d\omega} \]
Absolute Coverage Measurement for TCE

1. Gas-phase reference state:
   a. Use a calibrated diffusion vial
   b. Mass-flow controller

2. $\sigma_{abs}(\omega) = \frac{L_{abs}(\omega)}{\text{Path length}\times\text{Number density}}$

3. Peak cross section is $8.3 \times 10^{-21}$ cm$^2$/molecule

4. Integrated cross-section $\int \sigma(\omega) d\omega$ is conserved.
EW-CRDS spectra of TCE

\[ N_s = 1.41 \times 10^{14} \text{ molecules/cm}^2 \text{ and } \Theta = (74 \pm 2)^\circ \]
cis-DCE (dichloroethylene)

\[ N_s = 1.40 \times 10^{14} \text{ molecules/cm}^2 \text{ and } \Theta = (75 \pm 2)^\circ \]
trans-DCE

\[ N_s = 1.59 \times 10^{14} \text{ molecules/cm}^2 \text{ and } \Theta = (76 \pm 2)^\circ \]
Surface Orientation of TCE, c-DCE, and t-DCE

- Similar coverage: TCE 31% c-DCE 31% t-DCE 35%
- Orientation: Planar molecules lie flat at sub-ML coverage
- Major error source: Orientation
Limitations of a Molecular Orientation Measurement

1. Linear dichroism measures *average* orientation only.

2. If the dichroic ratio is expanded in spherical harmonics:

\[ \rho(\Theta) = \frac{A_s}{A_p} = \sum_{lm} d_{lm} Y_{lm} \]

only \( d_{20}(\Theta) \), the “order parameter” is obtainable:

\[ d_{20}(\Theta_{avg}) = \frac{(3\cos^2(\Theta_{avg})-1)}{2} \]

where \( \Theta_{avg} \) is average tilt angle of the transition moment.

3. Orientation distribution is unknown but can often be inferred.

4. “Flat” orientation has minimal error.
H-atom-induced defects in amorphous Si

The Problem (so-called Staebler-Wronski effect):

Solar cells made from a-Si:H degrade rapidly from 12% to 8% efficiency.
The effect is reversed by heating to 150 °C.

Proposed mechanism:

\[
a-Si:H + hv \rightarrow e^- + h^+ \\
Si-H + e^-/h \rightarrow Si\cdot + H\cdot \\
k_i \quad H\cdot + Si-Si \rightarrow Si\cdot + Si-H \\
k_r \quad Si\cdot + Si\cdot \leftrightarrow Si-Si + H_2^* \\
\]

Electron/hole pair created
Recombination generates H\cdot
H atoms are very mobile
“Dangling bond” defect is paired with H-atom and is also mobile

We apply a well-characterized H-atom beam to an a-Si:H film on a folded resonator.

This decouples the H-atom generation step from the H-atom reactions.

Using EW-CRDS, we obtain absolute values of \( k_i \), \( k_r \), and \( D \), the diffusion coefficient.
Experimental Details

Hot-wire CVD is used to grow a-Si:H from SiH$_4$.

Heated tube with stable H$_2$ flow creates the H-atom beam.

H-atom flux varies with film-source distant.

Film thickness = 60 nm ; Temp fixed at 150 °C.
Measured Results

Each exposure has a different H-atom flux.
Top plot is S-polarization; Bottom plot is P-polarization.
Last two fluxes recheck first and last case.
Note S-polarized > P-polarized absorption

$$N_{db}^{ss} \sim (F_H)^{1/3}$$
1. H-atoms diffuse rapidly, reaching a uniform density in ~ 1 sec.

2. Only a small fraction react (~1%). The majority simply diffuse out.

3. The small fraction insert into weak Si-Si bonds - but are still mobile.

4. The dB defects couple in a binary reaction that is reversible at 150 °C.
**EW-CRDS Detection of H-atom Interactions**

**Uptake** – Kinetics dominated process. Average field in the film is used. Both insertion and dB-dB coupling.

\[
\frac{d\alpha(t)}{dt} = \sigma_{db} \int_0^h \Gamma(z) dz \left\{ \frac{k_i [Si - Si] \gamma F_H}{N_b} - k_r N_{db}^2 \right\}
\]

\( \Gamma(z) \) is the E-field enhancement

**Decay** is a diffusion dominated process. Spatial dependence of the field is used. Only insertion is relevant; H-atoms vent.

\[
\frac{d\alpha(t)}{dt} = \sigma_{db} k \left[ Si - Si \right] H_0 \int_0^h \Gamma(z) f(z, t) dz
\]

\( D_H \)
Diffusion coefficient, $D_b$ coupling, & Insertion rate constants

A weakly flux-dependent $D$ is found.

Magnitude $\sim 10^{-11}$ - neglect of diffusion in uptake.

Similar values reported. More accurate?

$$A(\Phi_H) = k_i [Si-Si] \gamma F_H \sigma_{db} \int_0^h \Gamma(z) dz$$

Linear with $F_H$

$H_0$ from uptake DE

$k_i[Si-Si]=\text{pseudo first order}$

$1/k_i[Si-Si]=\text{H-atom lifetime} \sim 10 \text{ s}$
Bulk vs Surface Response?

We expected a surface contribution.

No sign of the 30:1 P:S surface polarization ratio.

Measured S&P signals overlap when corrected for BULK field differences.

Early time points overlap when corrected for shallow BULK field differences.

We think H- on the surface rearranges/accommodates rapidly between impacts.
Summary

**Monolithic resonators** provides many advantages:
- High sensitivity
- Polarized measurements
- In-situ operation
- Design flexibility

The Future:

- Absolute surface reaction kinetics
- Spectroscopy, growth, and reactions of oxides
- Reactions in and on thin films
- Applications to:
  - Atomic layer deposition
  - Catalysis
  - Solar cells (cont.)
  - Biosensing
  - ....
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