

Fundamental studies of radiation damage mechanisms in wide-band-gap semiconductors

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with

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Acknowledgements:

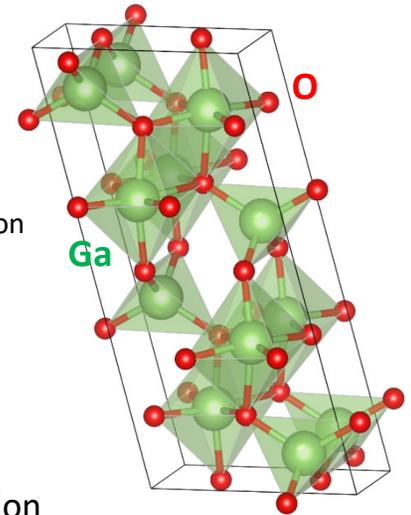
Sai Mu, Mengen Wang, J. Lyons, D. Wickramaratne, J. Speck

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Fundamental studies of radiation damage mechanisms

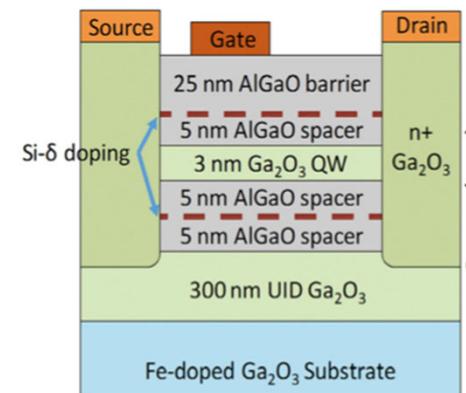
Computational research on the following research topics:

- **1. Point defect formation and temporal evolution**
 - Formation energies of relevant point defects
 - Motion of point defects during or right after the irradiation event
 - first-principles calculations of migration barriers, dissociation energies, and barriers to defect annihilation
- **2. Fundamental studies of defect formation mechanisms**
 - Develop formalisms to address the mechanisms that take place during excitation
 - Impact of presence of large concentrations of electron-hole pairs
 - Building on methodology for carrier capture
- **3. Role of pre-existing defects**
 - Examine whether preexisting defect states may act as nucleation sites for damage generation
- **4. Connecting to experimental characterization**
 - Defect signatures that can be directly compared with experiment and will enable the identification of defects
 - optical transitions and lineshapes
 - hyperfine parameters
 - vibrational frequencies
 - activation energies for deep-level transient spectroscopy
- **5. Effects of electric fields**



Materials: GaN, Ga₂O₃; SiO₂

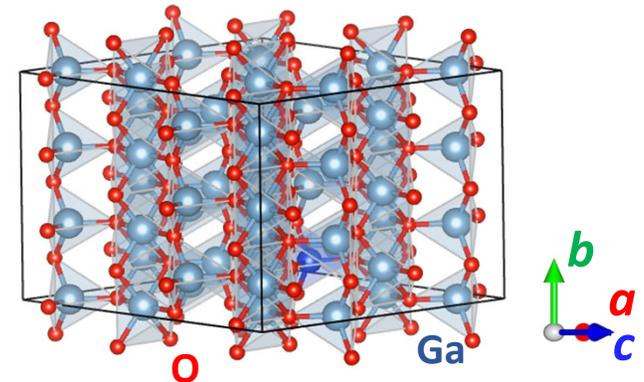
Excellent materials for high-frequency and high-power electronics



Computational approach

- Density functional theory (VASP)
- Monoclinic β -Ga₂O₃
 - Hybrid functional, $\alpha=0.32$
- GaN
 - Hybrid functional, $\alpha=0.31$

Ga₂O₃ 120-atom 1×3×2 supercell



Defect formation energy: *e.g.*, vacancy in Ga₂O₃

$$E^f(V_{\text{Ga}}^q) = E_{\text{tot}}(V_{\text{Ga}}^q) - E_{\text{tot}}(\text{Ga}_2\text{O}_3) + \mu_{\text{Ga}} + q(E_{\text{F}} + E_{\text{VBM}}) + \Delta_q$$

$E_{\text{tot}}(V_{\text{Ga}}^q)$ - total energy of V_{Ga} in charge state q in the supercell;

$E_{\text{tot}}(\text{Ga}_2\text{O}_3)$ - total energy of the bulk cell;

E_{F} - Fermi energy, referenced to VBM; Δ_q - finite-size correction term for charged defects.

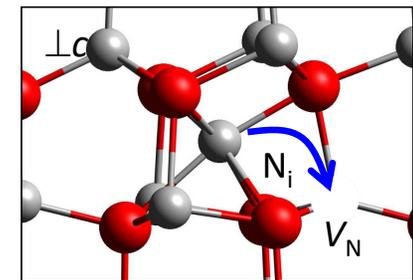
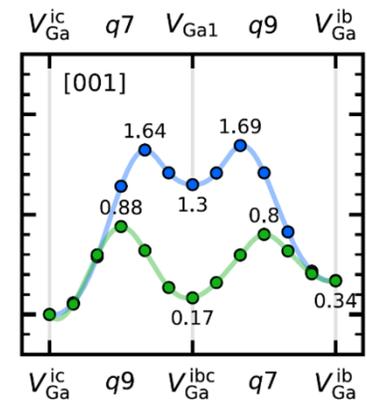
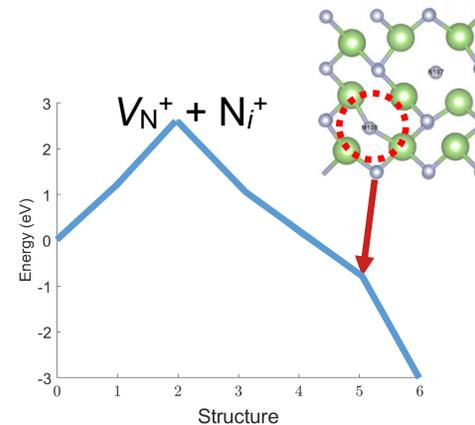
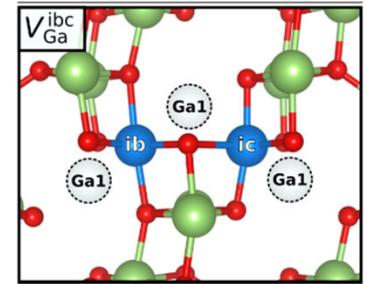
Migration: nudged elastic band method

G. Henkelman, B. P. Uberuaga, and H. Jansson, J. Chem. Phys. **113**, 9901 (2000).

Fundamental studies of radiation damage mechanisms

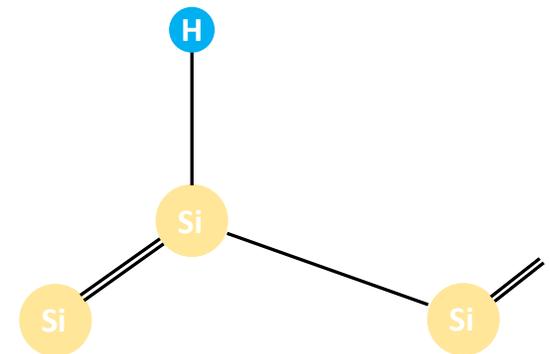
Point-defect formation and temporal evolution

- Calculated formation energies and migration barriers of all relevant point defects in GaN and Ga₂O₃
 - Discovered “three-split gallium vacancy”, which enables diffusion of Ga species in Ga₂O₃
 - Y. K. Frodason, J. B. Varley, K. M. H. Johansen, L. Vines, and C. G. Van de Walle, Phys. Rev. B **107**, 024109 (2023).
- Systematic study of point-defect motion during or right after the irradiation event
 - Defects can anneal out on short time scales
 - Calculate barriers to defect annihilation
 - depend on the charge state of the defects!
 - Charge balance → attractive interaction
 - No barrier to recombination
 - Charge imbalance → repulsive interaction
 - Barrier to recombination
 - Explains difference in radiation hardness between GaN and ZnO



Mechanisms of bond dissociation

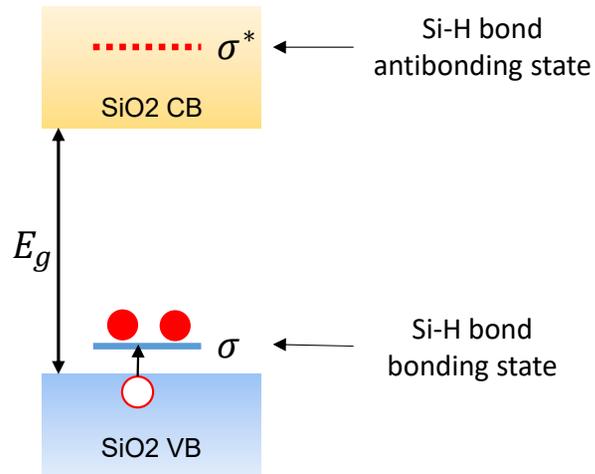
- Radiation events create large concentrations of electrons and holes
- Bond breaking in the presence of carriers
- Extensive experimental and theoretical studies in Si-SiO₂ MOSFETs
 - Si-H bond as test case
- Study process by which a hole or an electron enables the release of H from a hydrogen-passivated defect
- Calculate cross section
- Generalize to other hydrogenated defects



Two distinct mechanisms

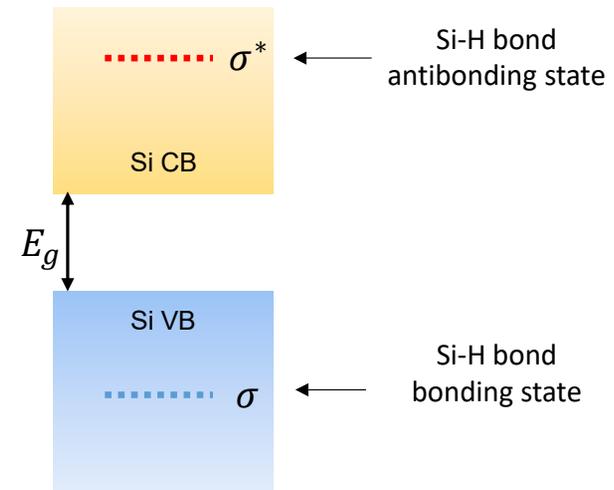
Charge capture into a state in the gap

Example: Si-H bond in SiO₂

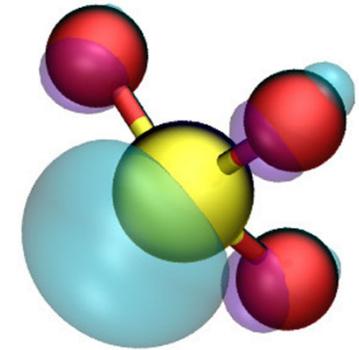


Charge capture into a resonant state

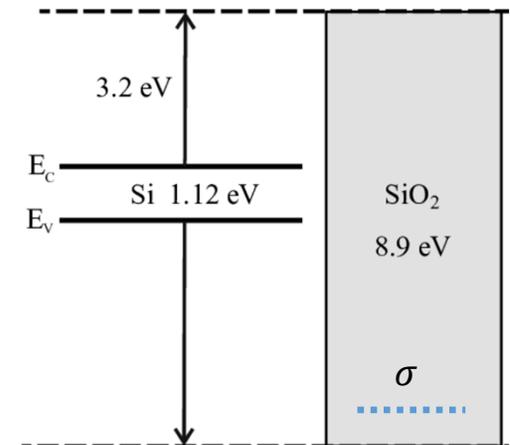
Example: Si-H bond in (or on) Si



Case 1: Charge capture at a localized state

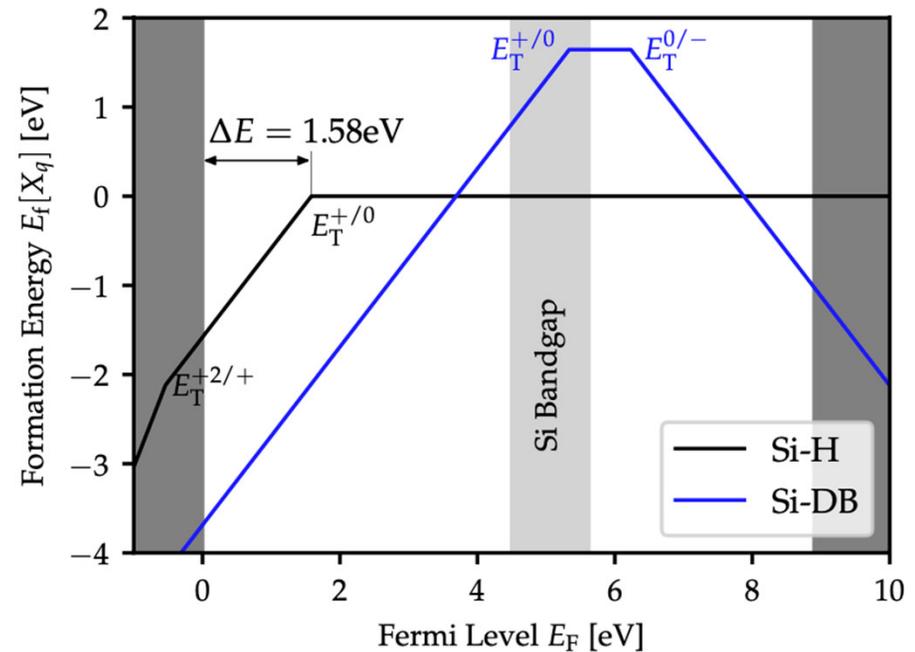


- ❑ **Hole-injection** in SiO_2 is known to produce Si dangling bonds (DB)
- ❑ Si DB formation is **correlated with proton release**
- ❑ Si-H bond is resonant with the Si valence band,
but **within the SiO_2 bandgap**
- ❑ Dissociation mechanism by **nonradiative capture via multiphonon emission**



Charge-state transition levels

- Si-H bond has a hole trap level at $\varepsilon(+/0) = 1.58 \text{ eV}$ above the SiO_2 VBM
 - Able to capture a hole from the VBM
- Si-DB has both hole and electron trap levels in the vicinity of the band edges of the Si channel
 - Can act as an amphoteric charge trap



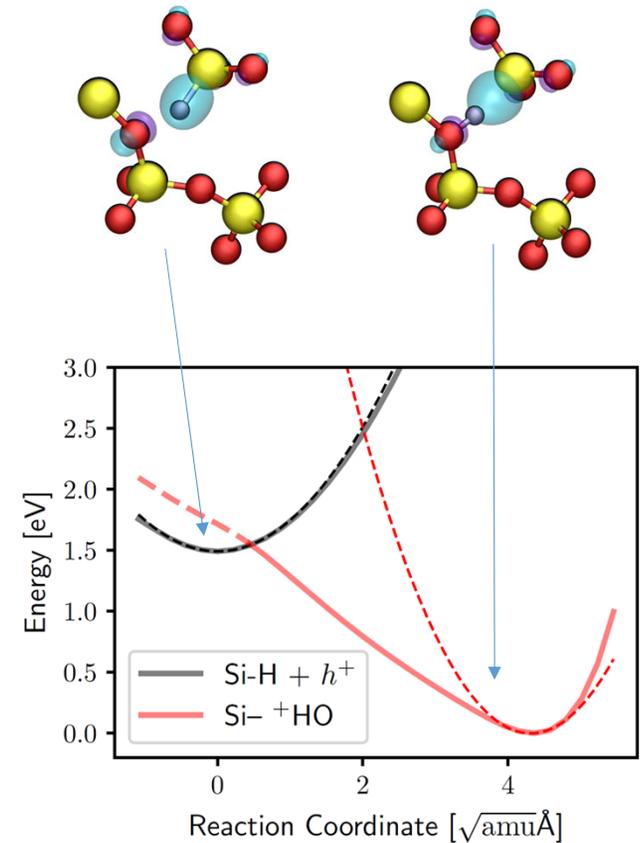
Charge capture process

□ Nonradiative Capture via Multiphonon Emission

- Holes are captured from the SiO_2 valence band
- CC diagram shows **low transition barrier** → **Si-H bond breakage**
- **H^+ binds to bridging O atom** nearby, but still interacts with the Si dangling bond

□ Subsequent H^+ hopping away from the Si dangling bond

- **Nudged elastic band calculations**
- Migration barrier of **$\sim 0.6\text{eV}$**
- **H^+ easily diffuses** away and leaves Si DB behind



Charge capture process

Determination of the capture cross-section (CCS)

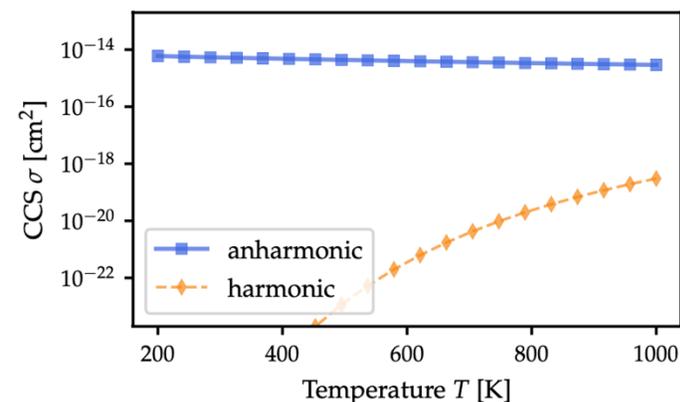
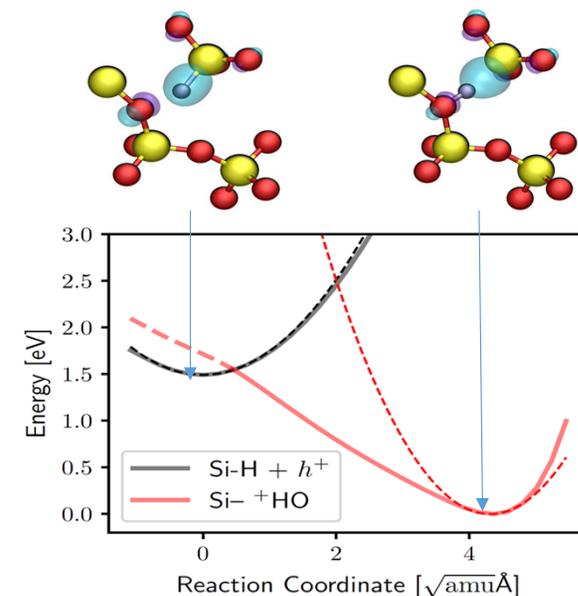
- MPE capture rate given by Fermi's Golden Rule

$$C = \frac{2\pi}{\hbar} V |\langle \psi_f | \frac{\partial \hat{H}}{\partial Q} | \psi_i \rangle|^2 \sum_{\alpha, \beta} p_{\alpha}(T) |\langle \eta_{f\beta} | \hat{Q} | \eta_{i\alpha} \rangle|^2 \delta(E_{i\alpha} - E_{f\beta})$$

- Experimentally given as an **effective cross-section**

$$\sigma = \frac{C}{v_{th}} = \frac{C}{\sqrt{k_B T / m^*}}$$

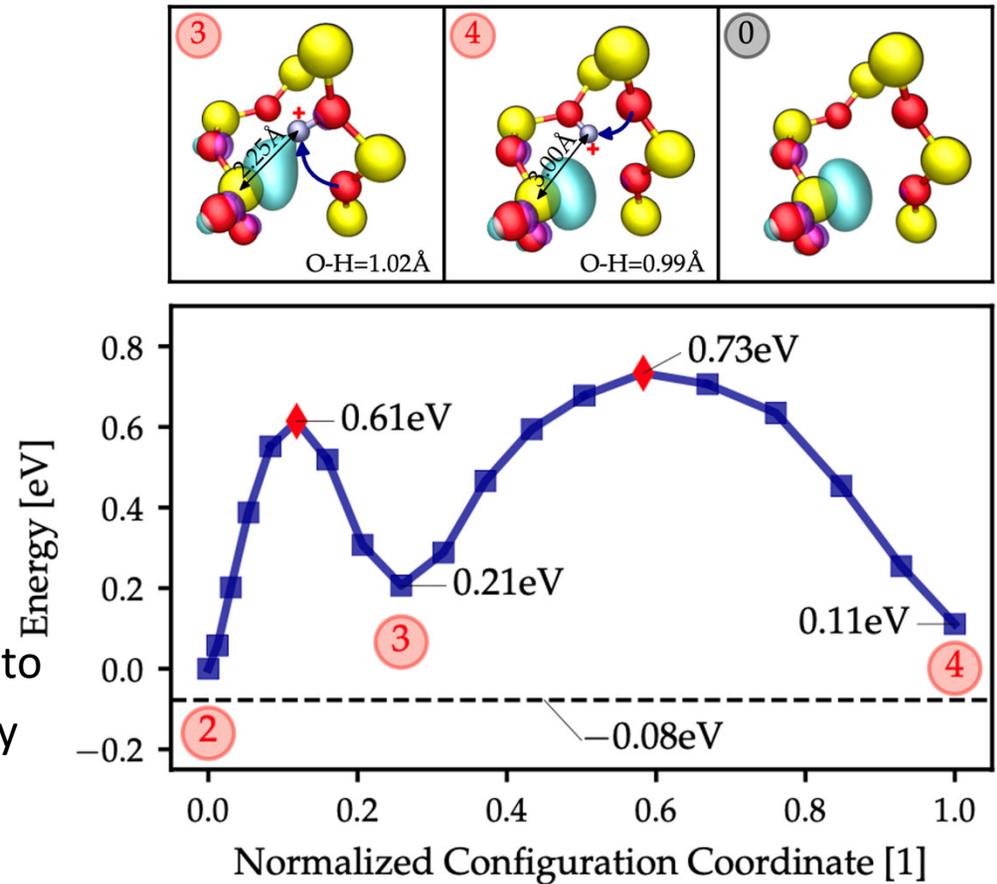
- **Capture cross section is almost temperature-independent** due to the low transition barrier
- Calculated CCS in good agreement with **experimental CCS of 10^{-15} - 10^{-14}cm^2** for neutral hole traps [1]
- Importance of anharmonicity!
- Much larger CCS than for neutral electron traps (10^{-17} - 10^{-18}cm^2)



[1] V. V. Afanas'ev and A. Stesmans, Europhys. Lett. **53**, 233 (2001).

H⁺ Migration process

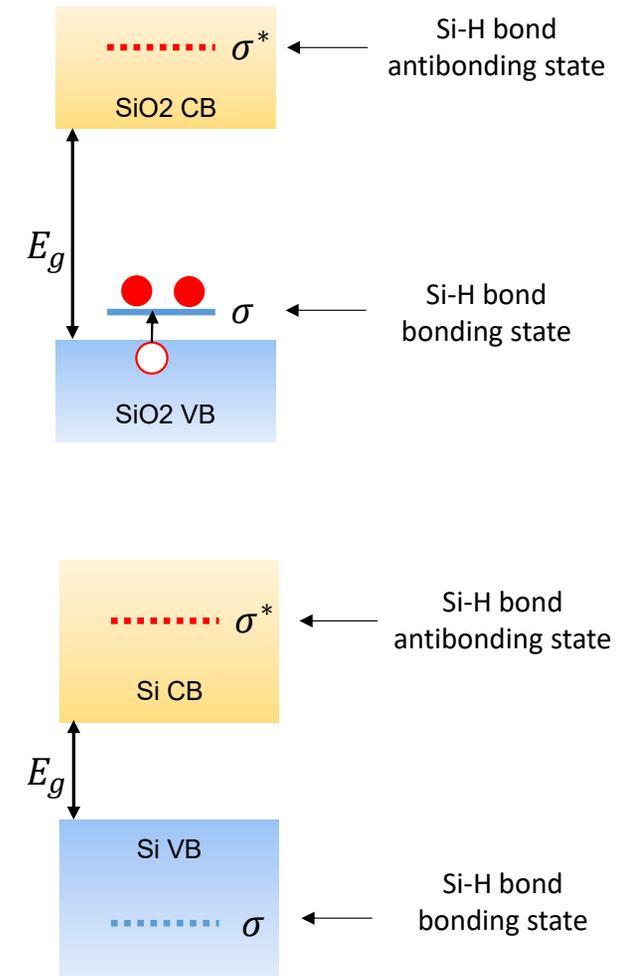
- After bond dissociation, still interaction between DB and H⁺
- Investigated migration path until H⁺ is no longer bound to the DB site (state 4)
- Barriers can be easily overcome at room temperature
- Therefore, hole capture at Si-H bond leads to the release of H⁺, which then diffuses freely throughout the oxide



Case 2: Resonant state

□ If a bonding or antibonding state is resonant with VB or CB, can a charge carrier get captured, leading to dissociation?

- These resonant states do not exist as isolated states
- Instead, they are hybridized (or resonant) with continuum levels
- Cannot readily identify the antibonding state in the band structure
- In addition, energy relaxation times for electrons in CB states are very fast (~ 10s of femtoseconds!)
- Electron does not stay in antibonding state long enough to allow for hydrogen to move
- However, we know from experiments that dissociation does occur!



Most detailed experimental evidence: STM experiments

- Experiments indicate the existence of a single-electron-driven bond dissociation process
 - Scanning tunneling microscopy measurements on H-passivated Si surfaces [1]
 - Low-energy electron injection (4-12 eV) experiments on H-passivated Si surfaces [2]
 - Hot-electron injection experiments in MOS structures [3]
- All of them report a "threshold-like behavior" around 7 eV.

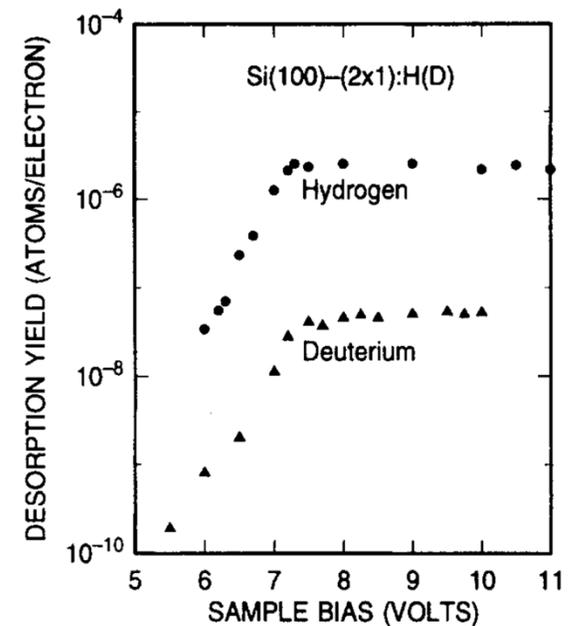


Fig. 1. Comparison of the STM-induced desorption yields of hydrogen and deuterium from Si(100)-(2 \times 1):H(D) as a function of the sample bias voltage. Figure from Ref. [1]

- [1] P. Avouris, R. E. Walkup, A. R. Rossi, T. C. Shen, G. C. Abeln, J. R. Tucker, and J. W. Lyding, Phys. Lett. **257**, 148 (1996).
[2] M. Bernheim, Surf. Sci. **494**, 145 (2001).
[3] D. J. DiMaria, J. Appl. Phys. **86**, 2100 (1999).

Previous approaches not successful

- Previous attempts to explain Si-H bond dissociation using first-principles calculations were not successful

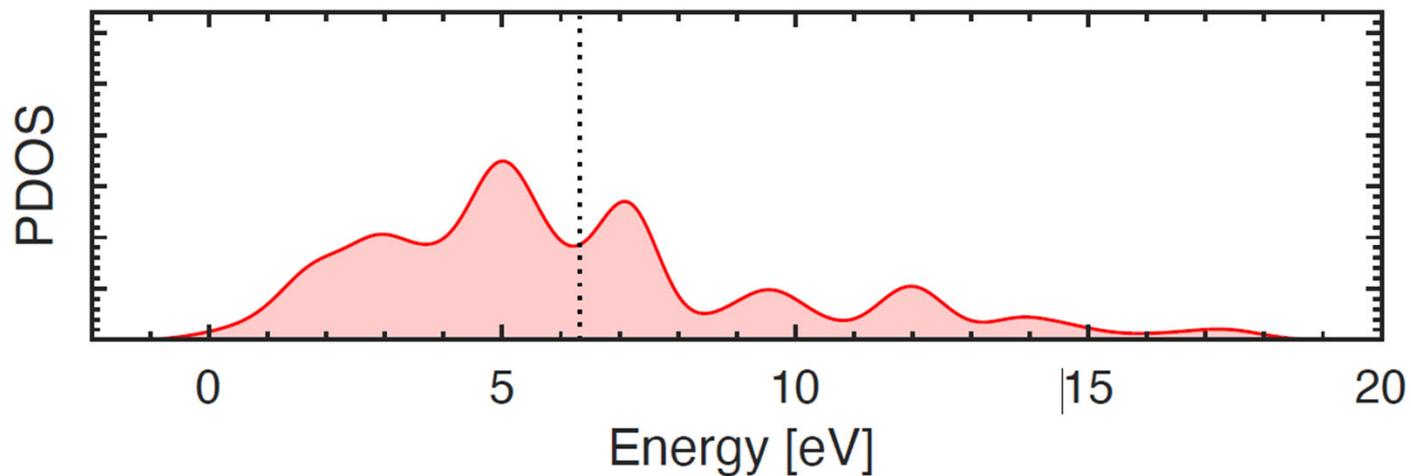
Ref	System	Method	Key messages
[4]	Molecule: Si ₄ H ₁₀ , Si ₇ H ₁₀ Slab: Si(111)-(1x1):H	Time-dependent DFT	<ul style="list-style-type: none">▪ Couldn't identify any localized states (σ, σ^*) for larger systems→ Couldn't obtain potential energy curve→ Couldn't provide any explanation for experimental observation (ex. 7 eV threshold, etc)
[5]	Molecule: Si ₄ H ₁₀ Intercage: Si(111)/SiO ₂ Si(100)/SiO ₂	Time-dependent DFT + Constrained DFT	
[6]	Slab: Si(001)-(2x1):H	Bethe-Salpeter Equation (BSE)	

[4] Y. Miyamoto and O. Sugino, Phys. Rev. B **62**, 2039 (2000).

[5] Y. Y. Liu, Z. Wei, S. Meng, R. Wang, X. Jiang, R. Huang, S. S. Li, and L. W. Wang, Phys. Rev. B **104**, 115310 (2021).

[6] N. P. Wang, M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B. **74**, 155405 (2006).

Problem with resonant states in first-principles calculations

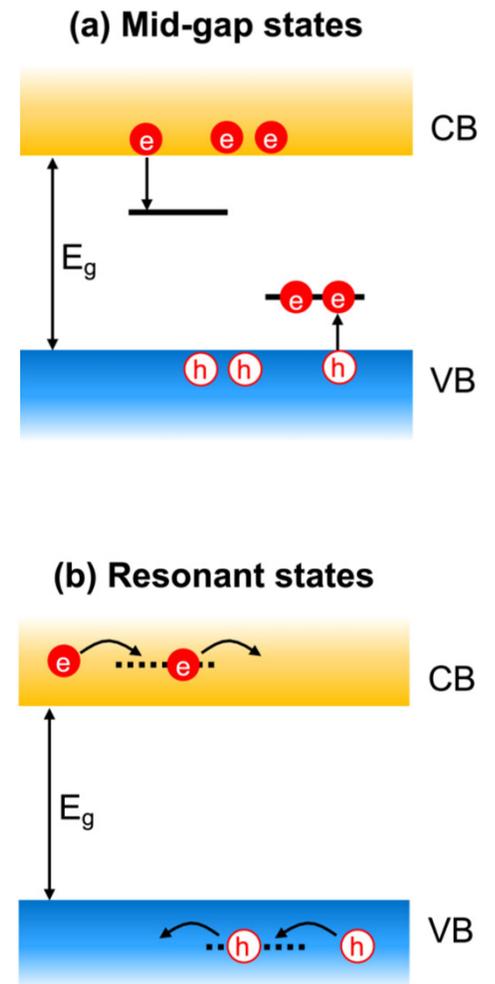


Projected density of states for the antibonding states of the Si-H bond in a bulk Si supercell

- Resonant states are not the eigenstates of the system.

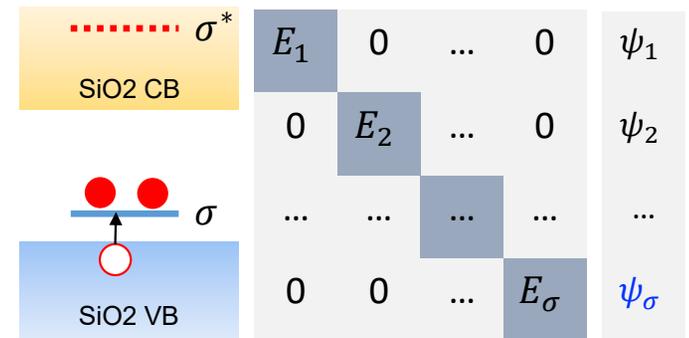
How to approach resonant states

- First, resonant states are not the eigenstates of the system. DFT calculations for resonant systems do not yield any localized states among their eigenstates, unlike mid-gap defect states.
- Second, due to the resonant nature, carriers cannot remain in these states for long, which is another key distinction from trapping in mid-gap states.



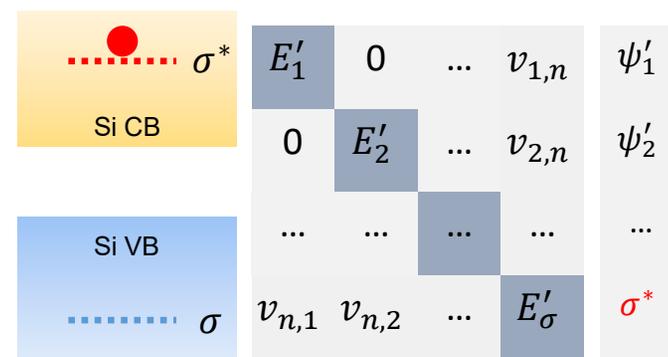
Re-visit the basic transition theory

- Two choices for describing transitions:
 - **Adiabatic states:** with varying nuclear coordinates, change their character constantly so as to remain eigenstates of the electronic Hamiltonian
 - Align with the concept of DFT eigenstates (diagonal H_e)
 - Suitable for the case where nuclear motion is small



Re-visit the basic transition theory

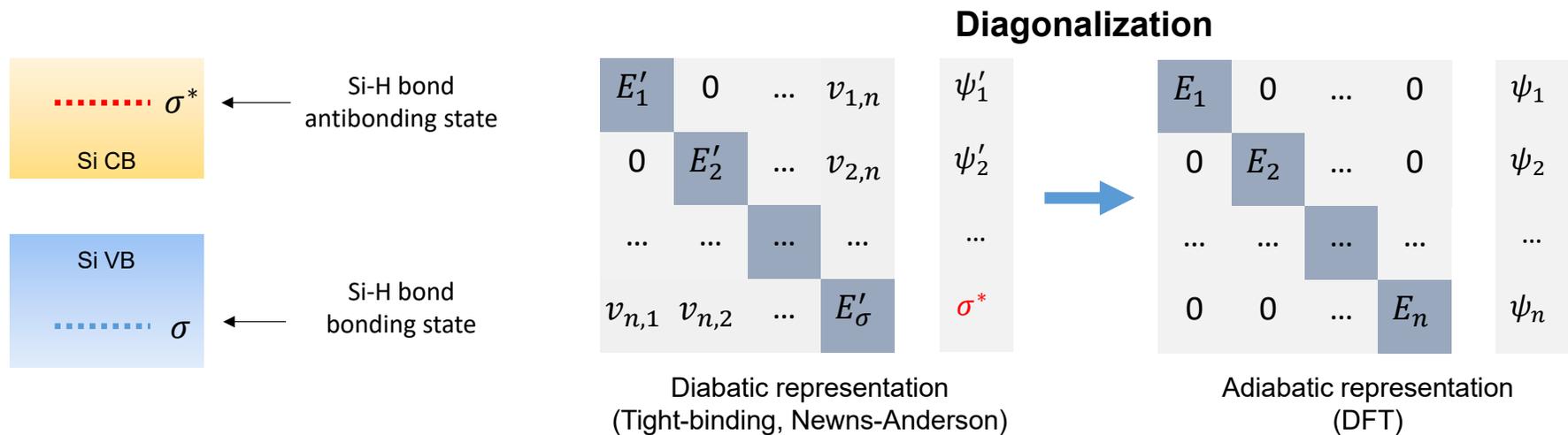
- Two choices for describing transitions:
 - **Diabatic states:** with varying nuclear coordinates, do not change their physical character as one moves along a reaction coordinate
 - Align with the concept of molecular orbitals (non-diagonal H_e)
 - Suitable for the case where nuclear motion is large



* Align with how chemists describe kinetics of reactions between molecules

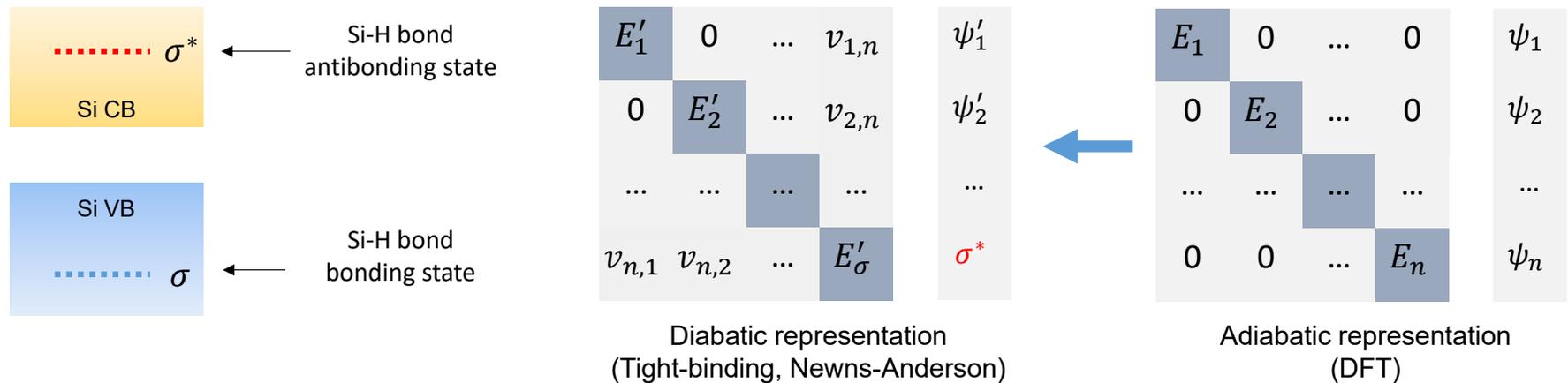
Problem of previous approaches

- Si-H bonding & antibonding states = molecular orbital states (correspond to diabatic states)
- These states are not “isolated” in Si (they are resonant)
- Off-diagonal (electronic coupling) term exists in electronic Hamiltonian



Problem of previous approaches

- What others have calculated with DFT: *Adiabatic* representation
- What we need: *diabatic* representation (to describe bonding/antibonding states, to draw potential energy curves, etc)
- **Goal: perform adiabatic-to-diabatic transformation**



How to obtain diabatic states (diabatization)

- What chemists do for diabatization:
 - Foster-Boys localization: Maximize the distance between charge centers

$$f_{\text{boys}}(U) = \sum_{A,B} |\langle \phi_A | \vec{\mu} | \phi_A \rangle - \langle \phi_B | \vec{\mu} | \phi_B \rangle|^2$$

- What condensed-matter physicists do:
 - Maximally Localized Wannier function: Minimizes the spread of the orbital

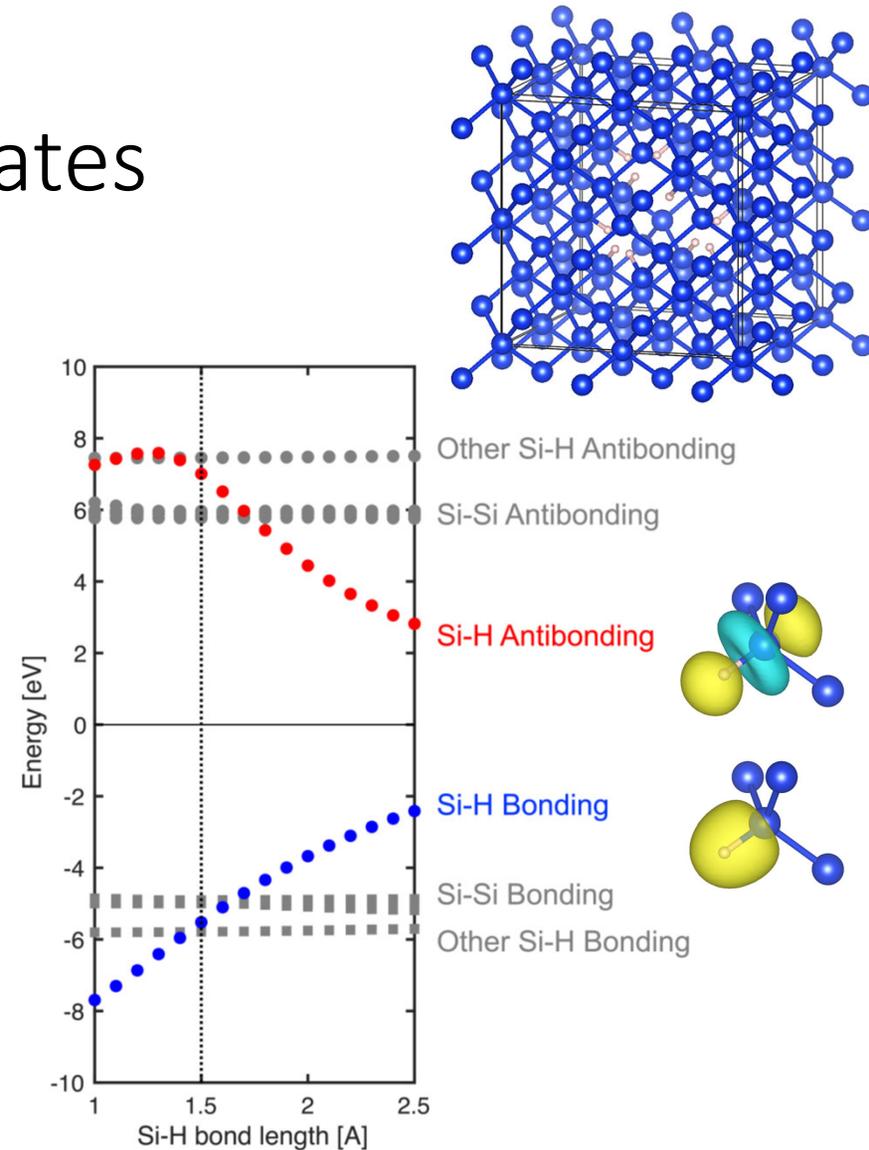
$$f_{\text{wannier}}(U) = \sum_i \langle \phi_i | r^2 | \phi_i \rangle - \langle \phi_i | r | \phi_i \rangle^2$$

“This turns out to be the solid-state equivalent of the Foster-Boys criterion of quantum chemistry” [7]

[7] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Rev. Mod. Phys. **84**, 1419 (2012).

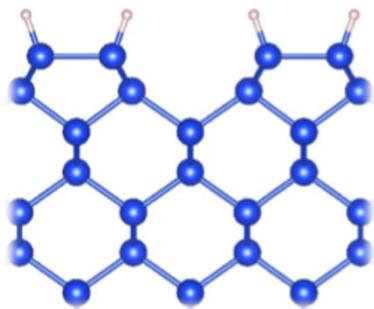
Energy level of Si-H bond states

- We can identify resonant “Si-H bond states”
 - Highly localized
→ describe strong local electron-lattice interaction
 - Physical interpretability
→ corresponds to molecular orbitals
 - Do not change character with varying nuclear geometry
→ aligns with the concept of *diabatic states*
 - Smooth energy level
→ Allow us to obtain smooth potential-energy surfaces and investigate associated nuclear dynamics

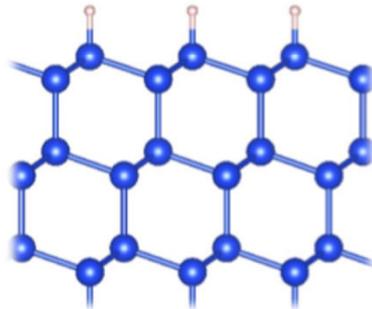


Energy level of Si-H bond states

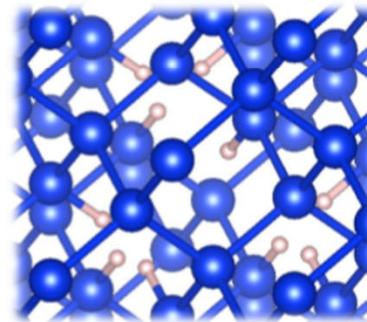
- We compared Si-H bonds in bulk and at surfaces
- Very similar energies, because the *local geometry* of these structures is nearly identical



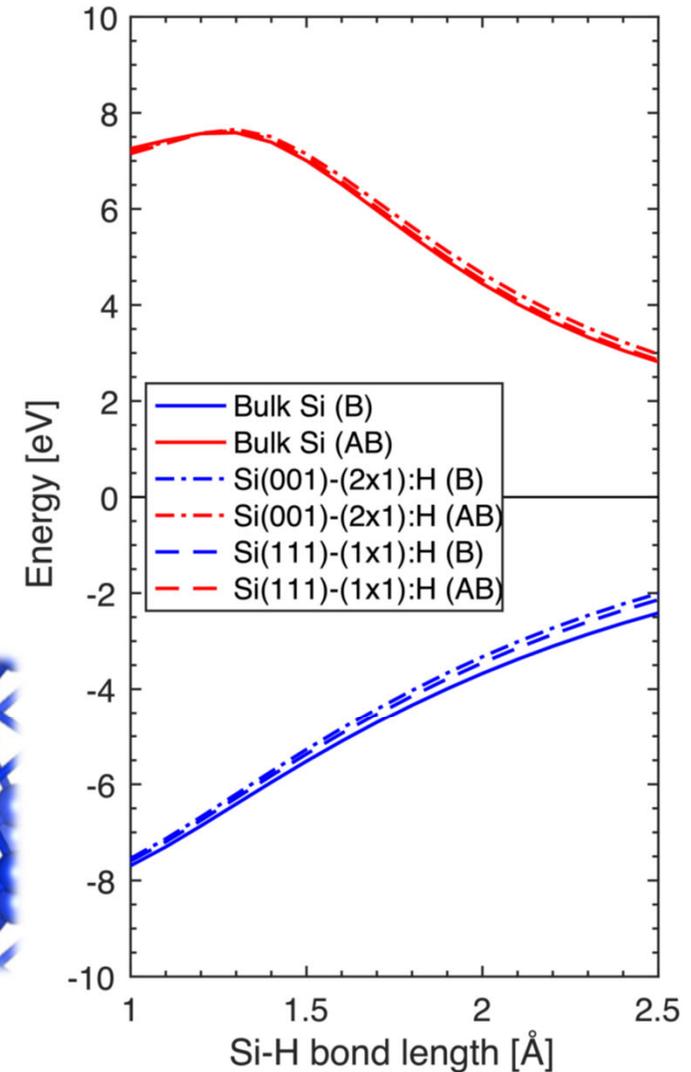
Si(100)-(2x1):H



Si(111)-(1x1):H

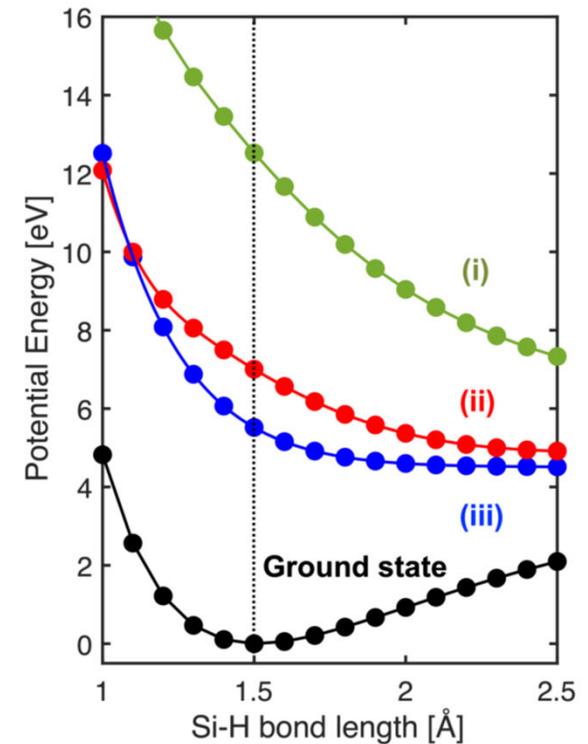
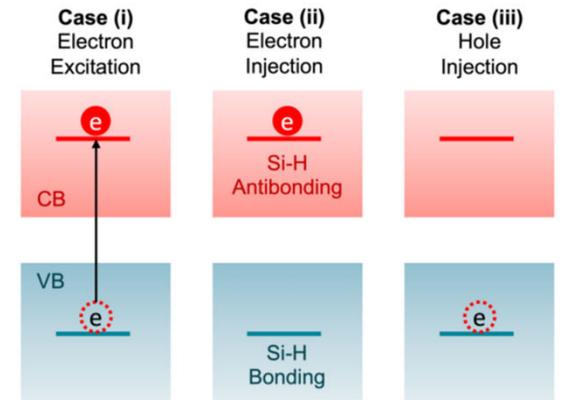


Bulk Si



Potential energy curves

- We investigate potential energy curves for three different excitation processes
 - Electron injection into Si-H antibonding state (**case ii, red curve**) explains experimentally observed 6~7 eV threshold for dissociation



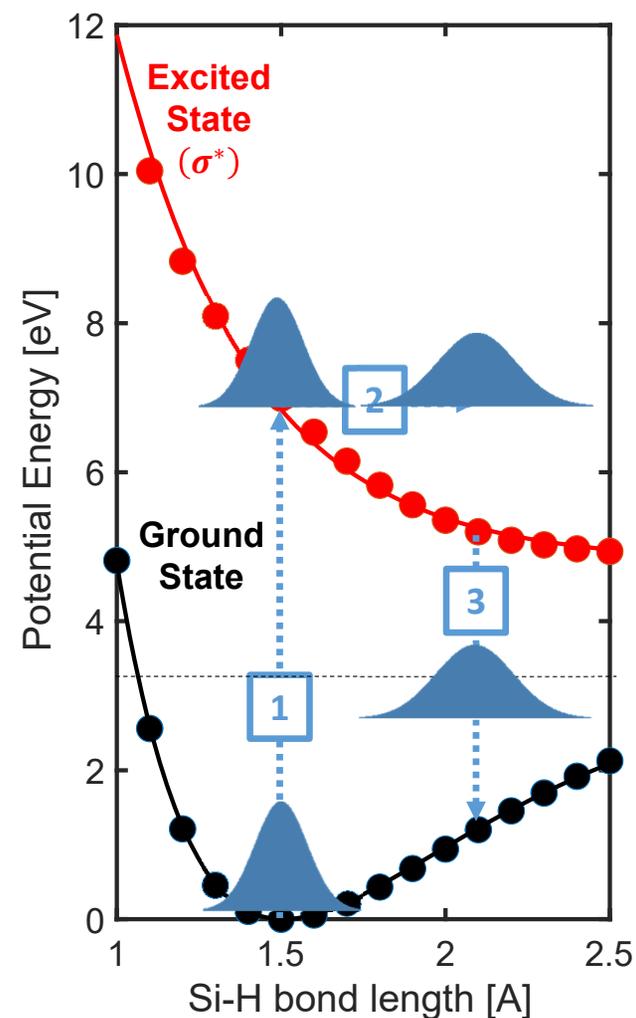
Nuclear dynamics

* Menzel-Gomer-Redhead (MGR) model [8-10]

- Solve time-dependent Schrödinger equation for H wavefunction (Ψ_H)

$$i \frac{\partial \Psi_H(z, t)}{\partial t} = \hat{H} \Psi_H(z, t), \quad \hat{H} = \frac{-\hbar^2}{2M_H} \nabla^2 + V_{g,e}$$

- At $t = 0$, switching from ground to excited-state ($V_g \rightarrow V_e$)
- For $0 < t < \tau_R$, Ψ_H evolves on the excited PEC
- At $t = \tau_R$, switching from excited- to ground-state ($V_e \rightarrow V_g$)
- For $t > \tau_R$, Ψ_H evolves on the ground-state PEC



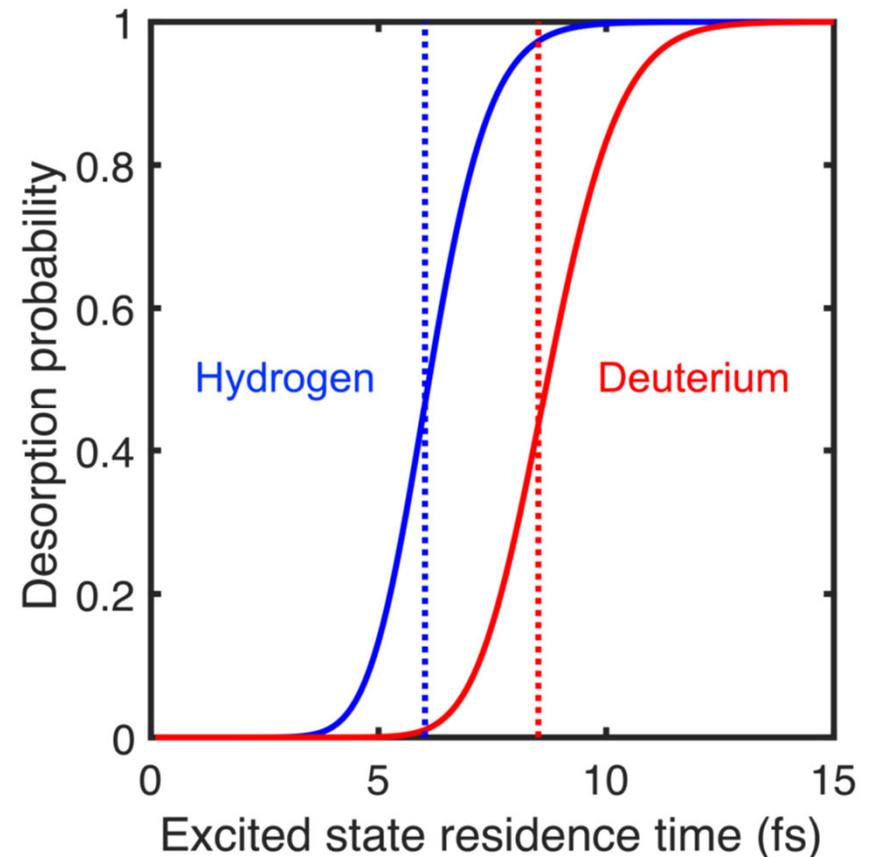
[8] D. Menzel and R. Gomer, J. Chem. Phys. **41**, 3311 (1964).

[9] P. A. Redhead, Can. J. Phys. **42**, 886 (1964).

[10] D. Menzel, Surf. Interface Anal. **38**, 1702 (2006).

Dissociation probability

- “Semi-classically” (dashed line)
 - Desorption probability is step function
- Quantum mechanics (solid line)
 - Desorption probability becomes smooth function
- Deuterium shows lower desorption probability because of slower propagation speed

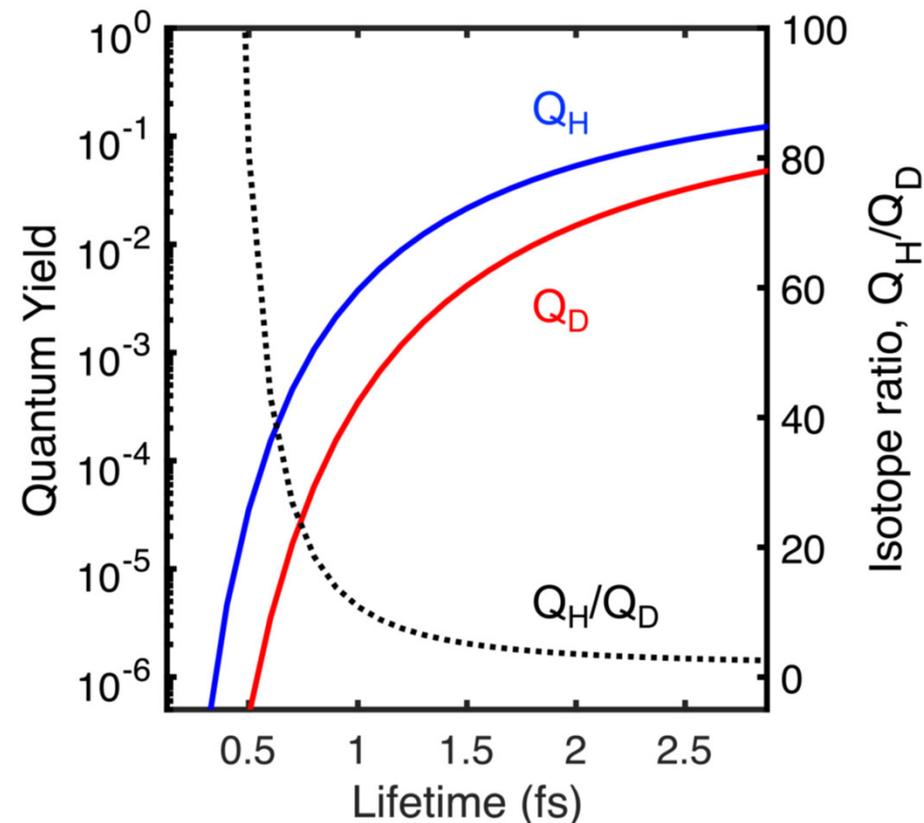


Quantum Yield

- Experimental results are the outcome of multiple events
 - Each event has different residence time
 - Need to consider the distribution of residence time

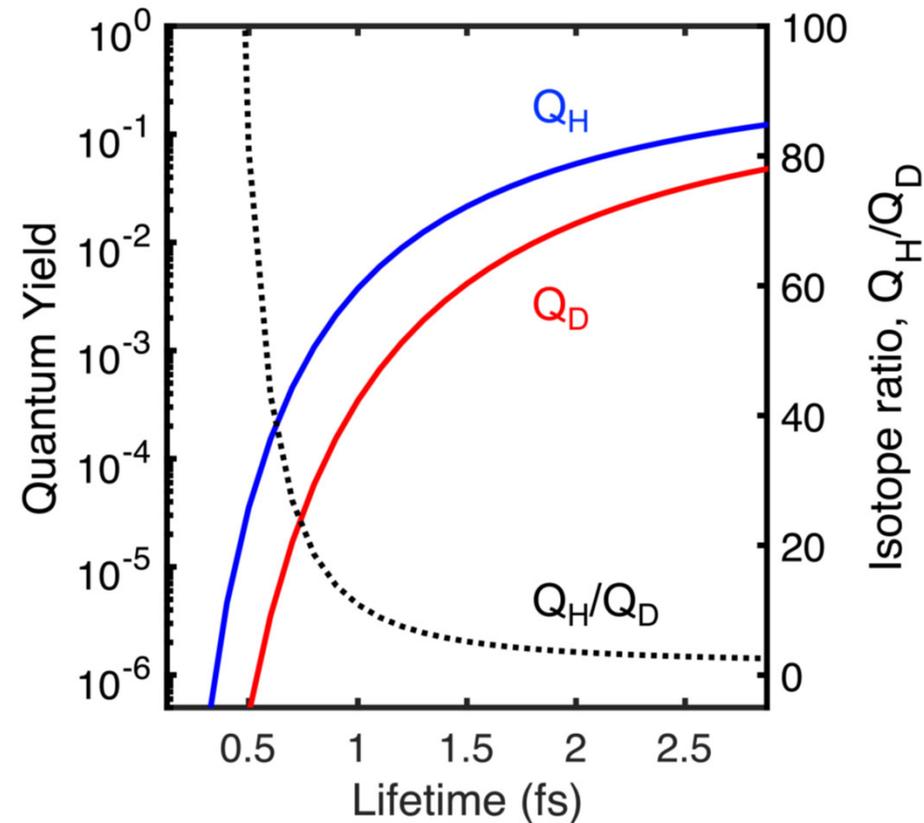
$$Q(\tau) = \frac{\int p(\tau_R) e^{-\tau_R/\tau} d\tau_R}{\int e^{-\tau_R/\tau} d\tau_R} \quad (7)$$

* Approach known as “incoherent averaging of quantum trajectories”



Quantum Yield

- STM papers report a large isotope effect
 - Reported isotope ratio: 50 ~ 200(Motivation for using deuterium instead of hydrogen for passivation)
- Indicates sub-femtosecond lifetime
 - typical time-scale for surface kinetic processes



Compare with STM desorption yield

- Desorption yield is proportional to the product of
 - Rate of electron injection into the surface state
 - Quantum yield

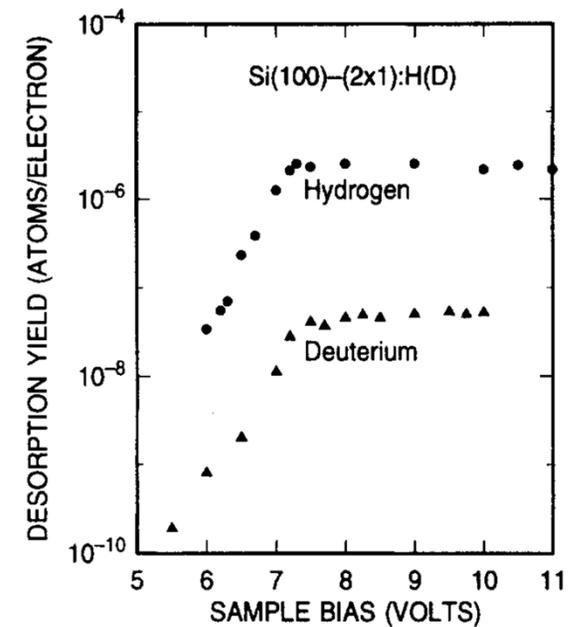
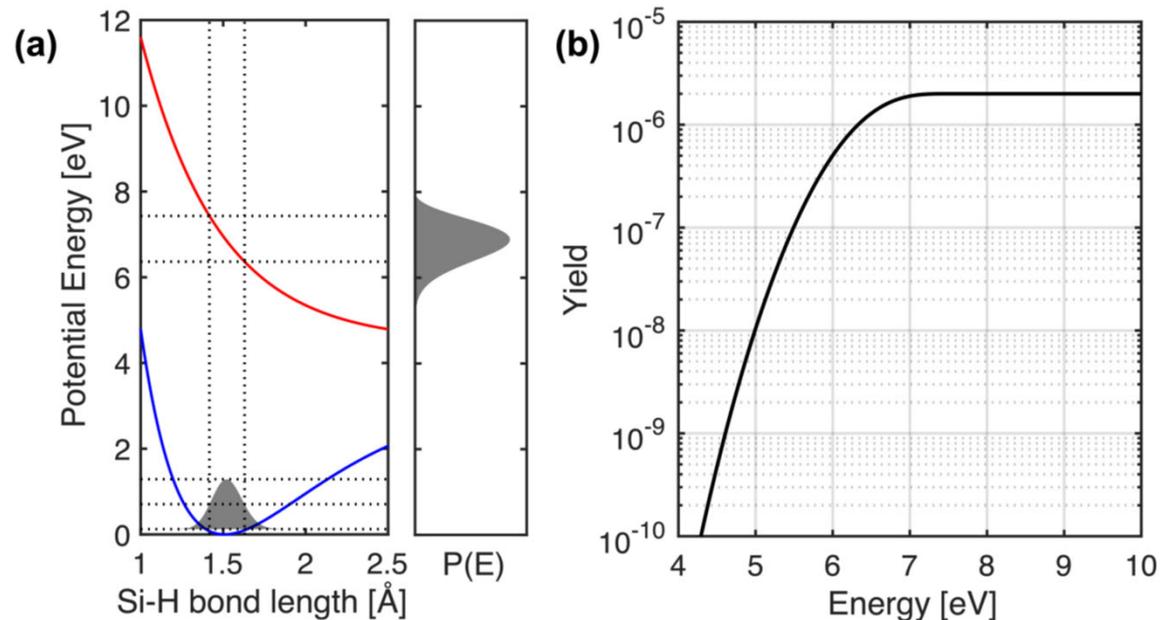


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Compare with STM desorption yield

- Si-H antibonding state energy is not a fixed value
- Distribution $P_{AB}(E)$ depends on the vibrational wavefunction
- Therefore, we can write

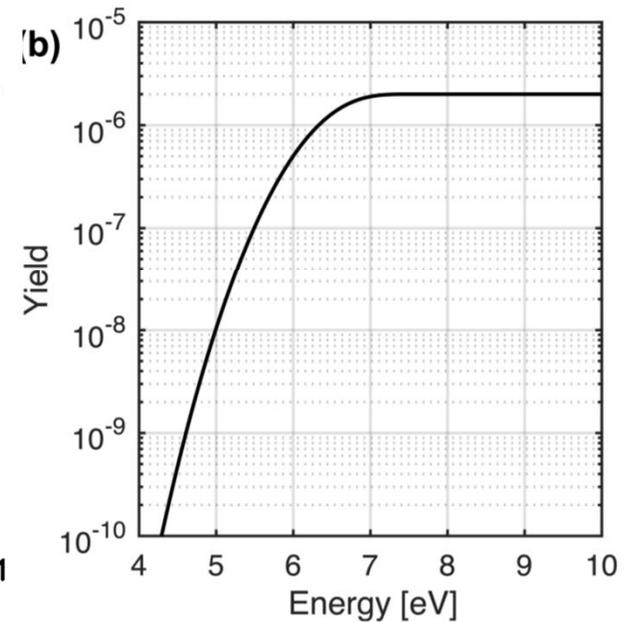
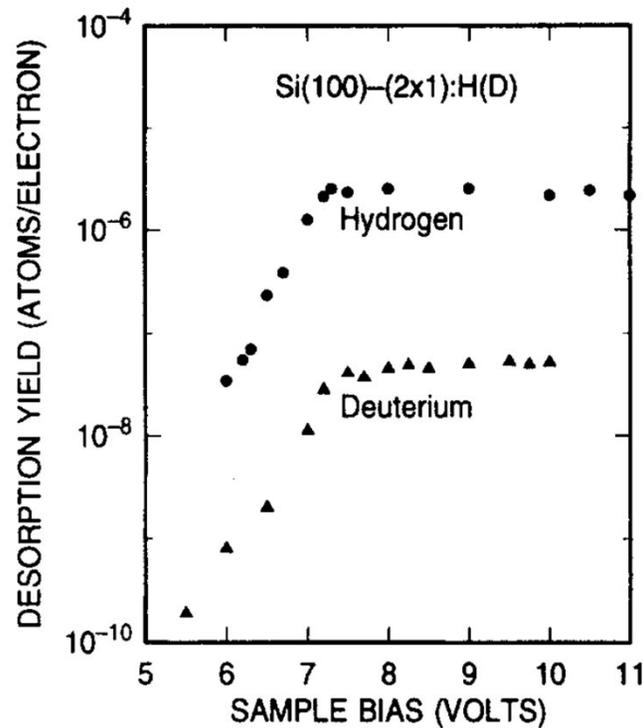
$$\text{Yield} \propto P_{\text{des}} \int dE P_{AB}(E)$$



Compare with STM desorption yield

Accomplishments:

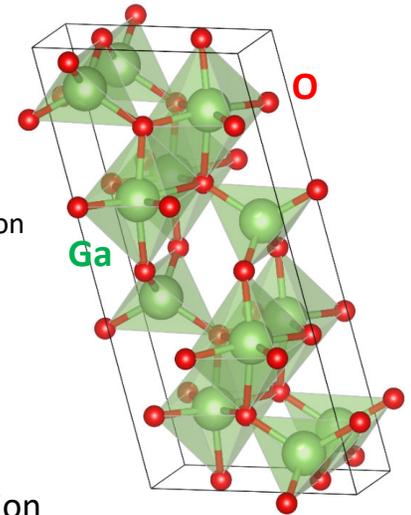
- First successful approach to model the dissociation process based on first-principles calculations
- Identified the origin of the 7eV threshold
- Dissociation can occur at lower bias!



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