

Degradation of the aluminum filters on SDO/EVE

Bobby Berg

with

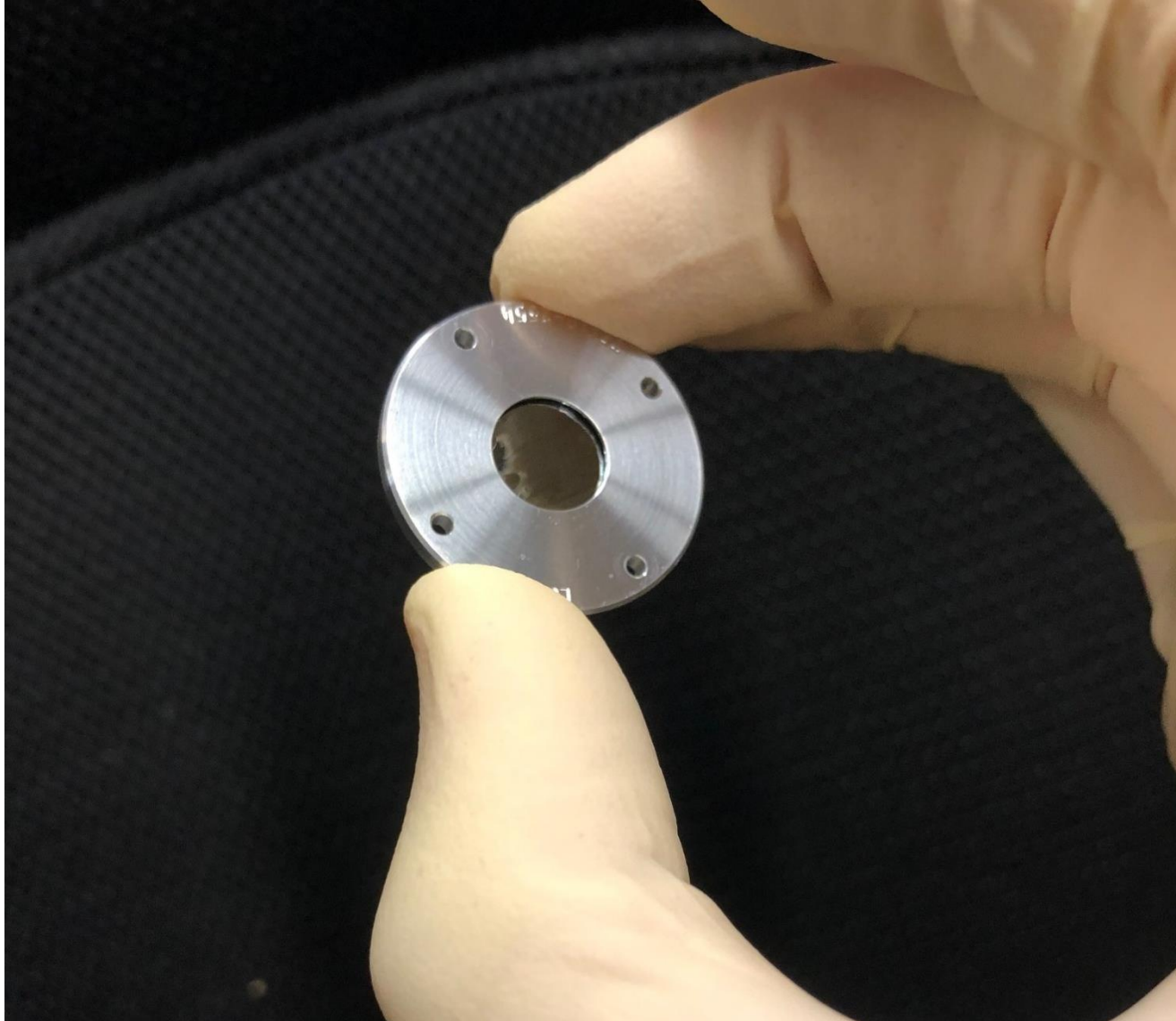
Charlie Tarrío and Tom Lucatorto
NIST

and

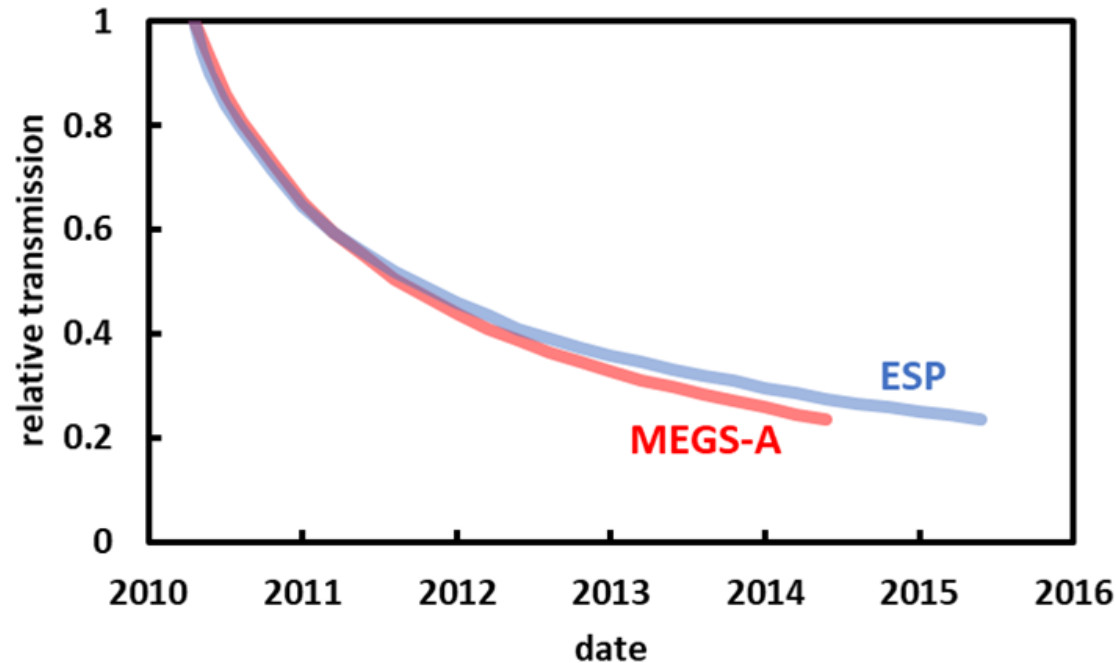
Frank Eparvier, Andrew Jones
Laboratory for Atmospheric and Space Physics
University of Colorado

SDO/EVE Science Team meeting
26 July 2023

Problem: Degradation of the aluminum filter



Problem: Degradation of the aluminum filter



The Al filter was used to select $\lambda = 30.4$ nm.

Q: How do we know the degradation occurred?

A1: Compared the primary filter to a reference filter with less exposure.

A2: Compared an SDO observation to one made with a sounding rocket.

Q: Why is this a problem?

A: Increased uncertainty, cost of recalibration by sounding rocket flights.

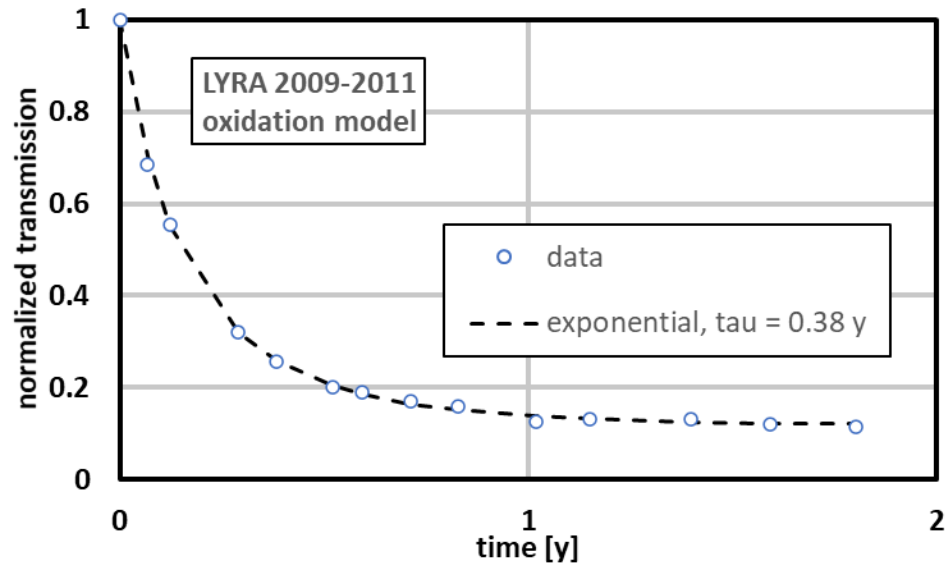
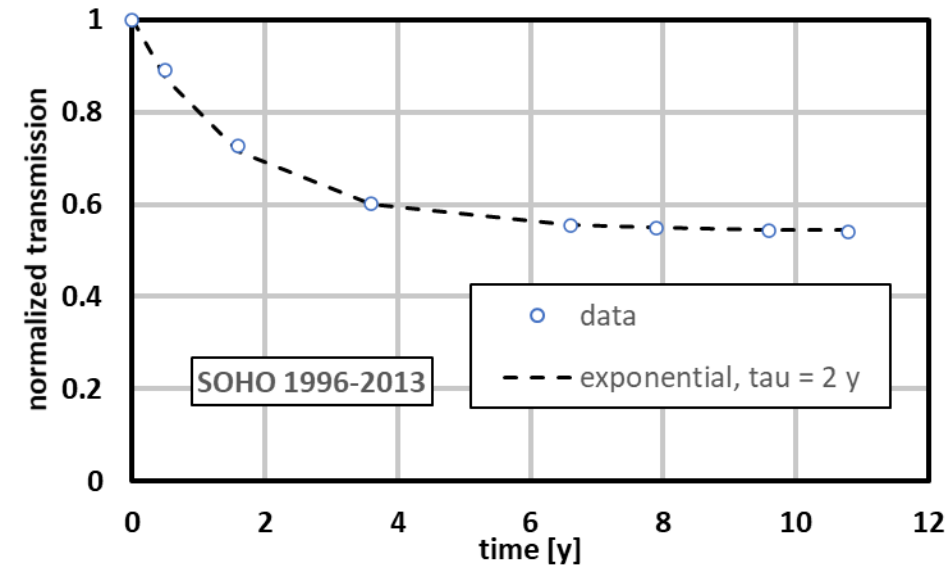
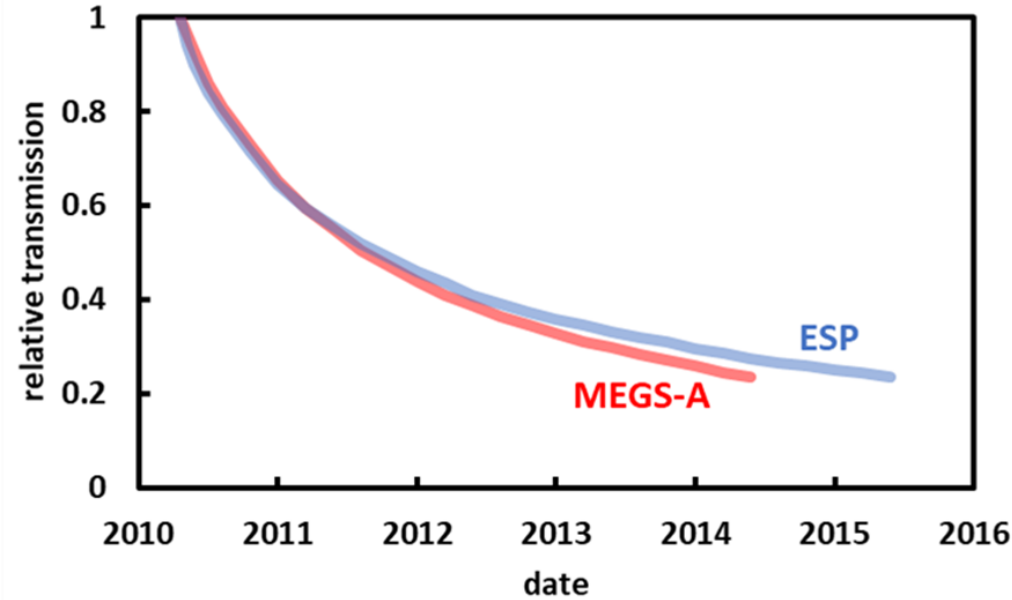
Q: What caused it?

A: Carbon is the usual cause.

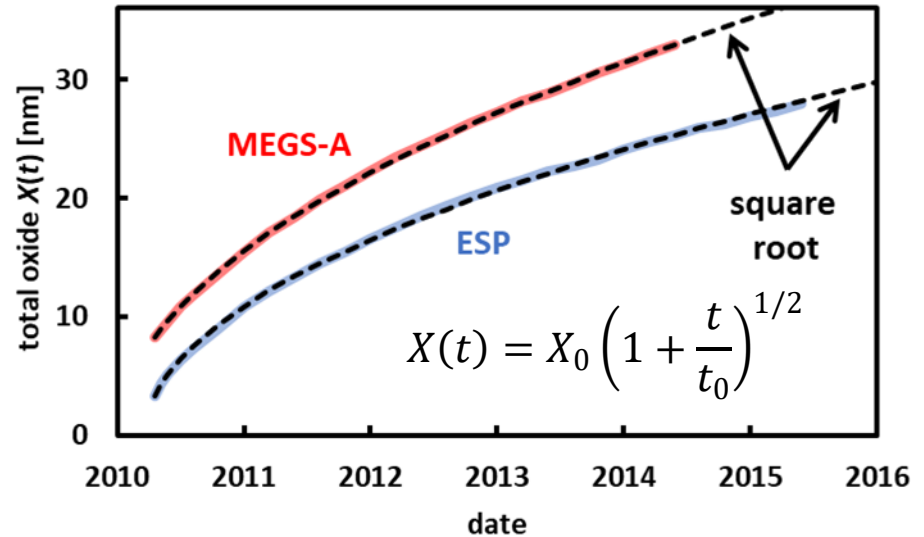
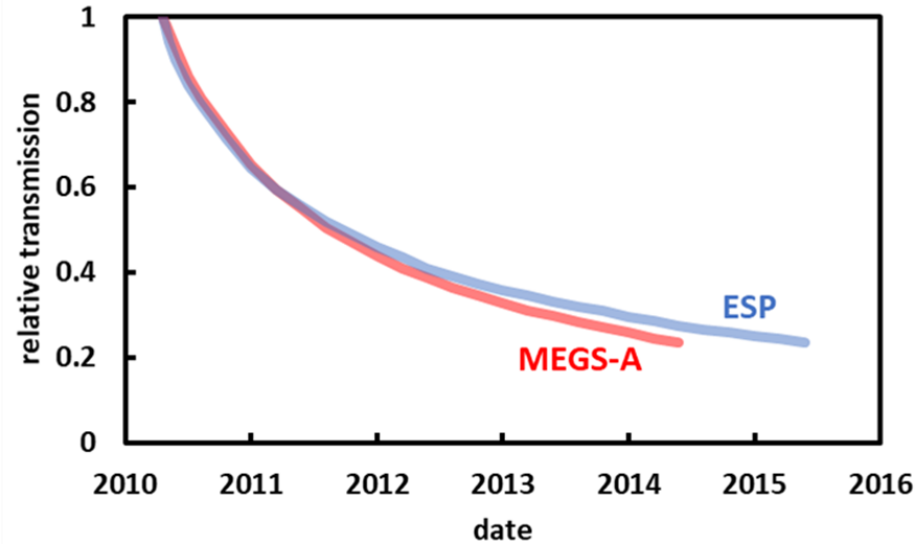
The usual suspect: Carbon

How carbonization occurs

1. Volatile organics outgas.
2. Organics condense on optics.
3. UV cracks the organics.
4. The carbon layer absorbs light.



The degradation on SDO was different



The satellite materials were chosen to minimize outgassing of organics.

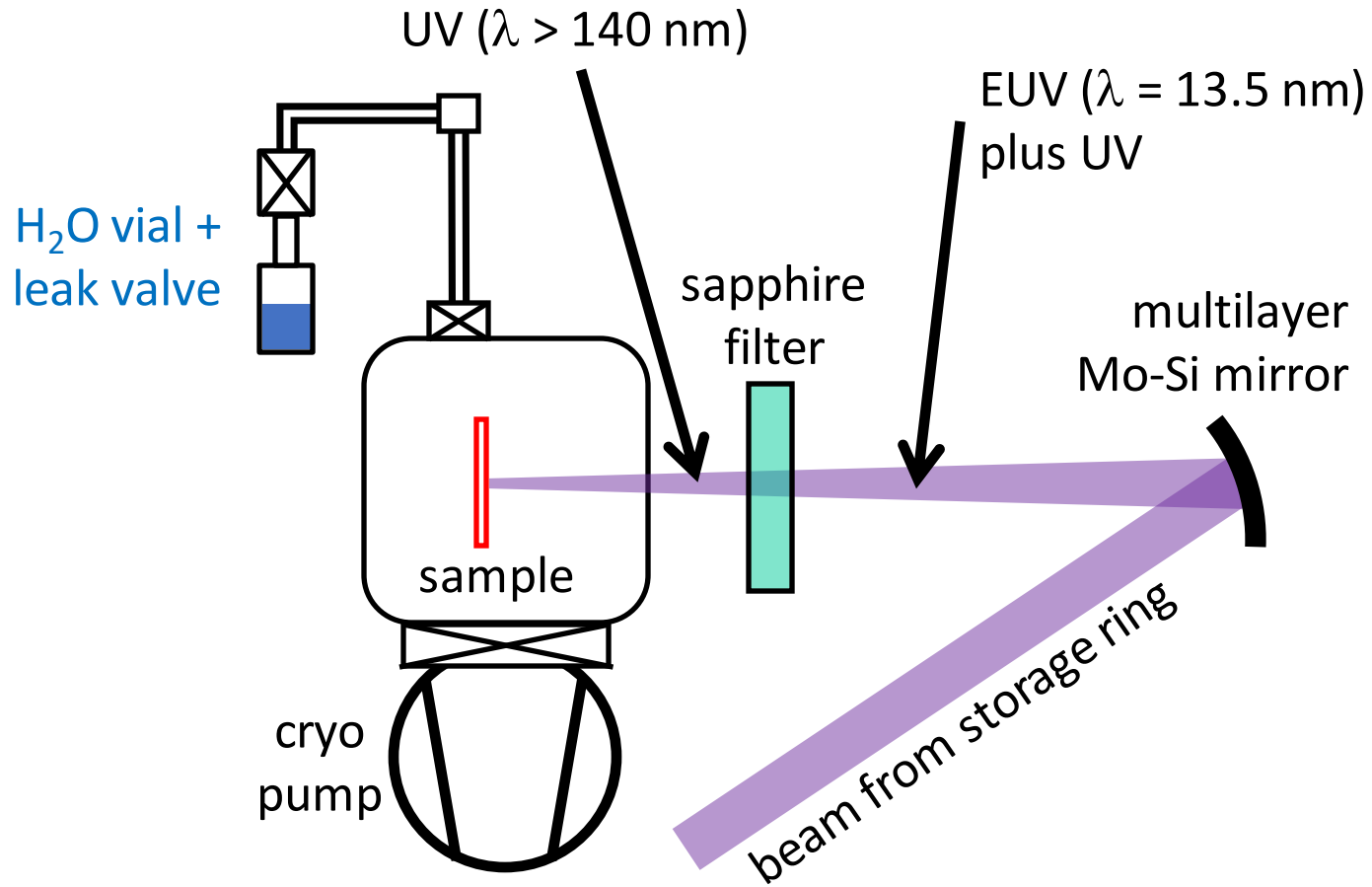
A nearby zirconium filter did not degrade.

The time dependence was square root, $t^{1/2}$, not exponential, $e^{-t/\tau}$.

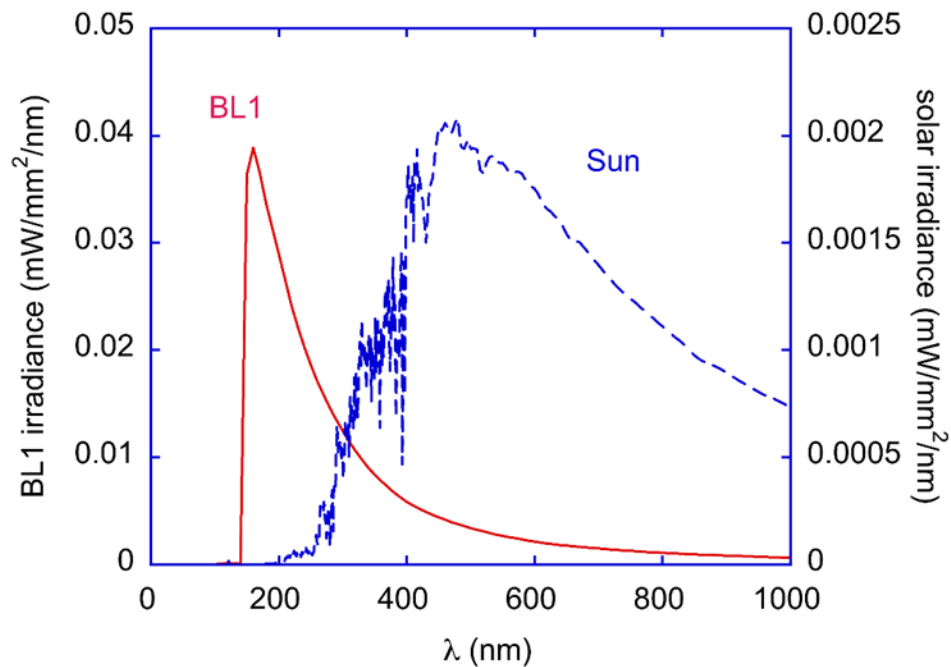
Aluminum oxide (Al_2O_3) can explain the degradation as well as carbon.

Water outgassing is always present, and $\text{Al} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3$.

SURF (synchrotron) Beamline 1a



SURF (synchrotron) Beamline 1a



Three challenges

What: Demonstrate that carbonization did not cause the SDO problem.

Why: Carbon has been the usual cause for degraded UV optics.

How: Expose Al samples to SURF in an atmosphere of 10^{-6} Torr toluene.

What: Demonstrate the possibility of UV-induced oxidation.

Why: 24 nm of Al oxide has never been grown at 300 K and low pressure.

How: Expose Al samples to SURF in a “humid” (10^{-6} Torr) atmosphere.

What: Model UV-induced oxidation

Why: Allow accurate comparison between SURF results and SDO data.

How: Combine photoemission, electron scattering, and oxidation.

The plan

SURF exposures and measurements of the oxide

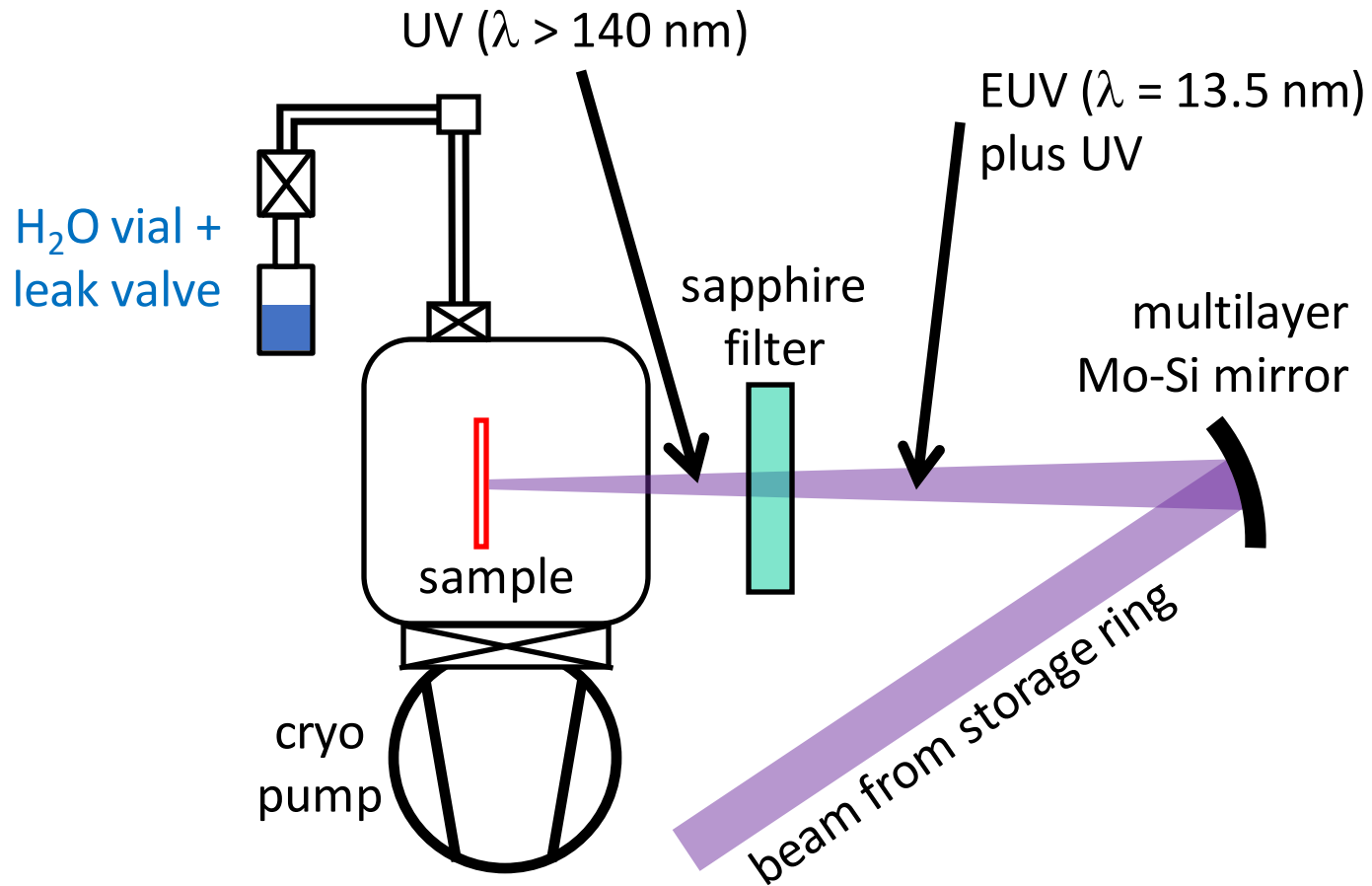
Modeling the oxide growth

Comparing the model to the measurements

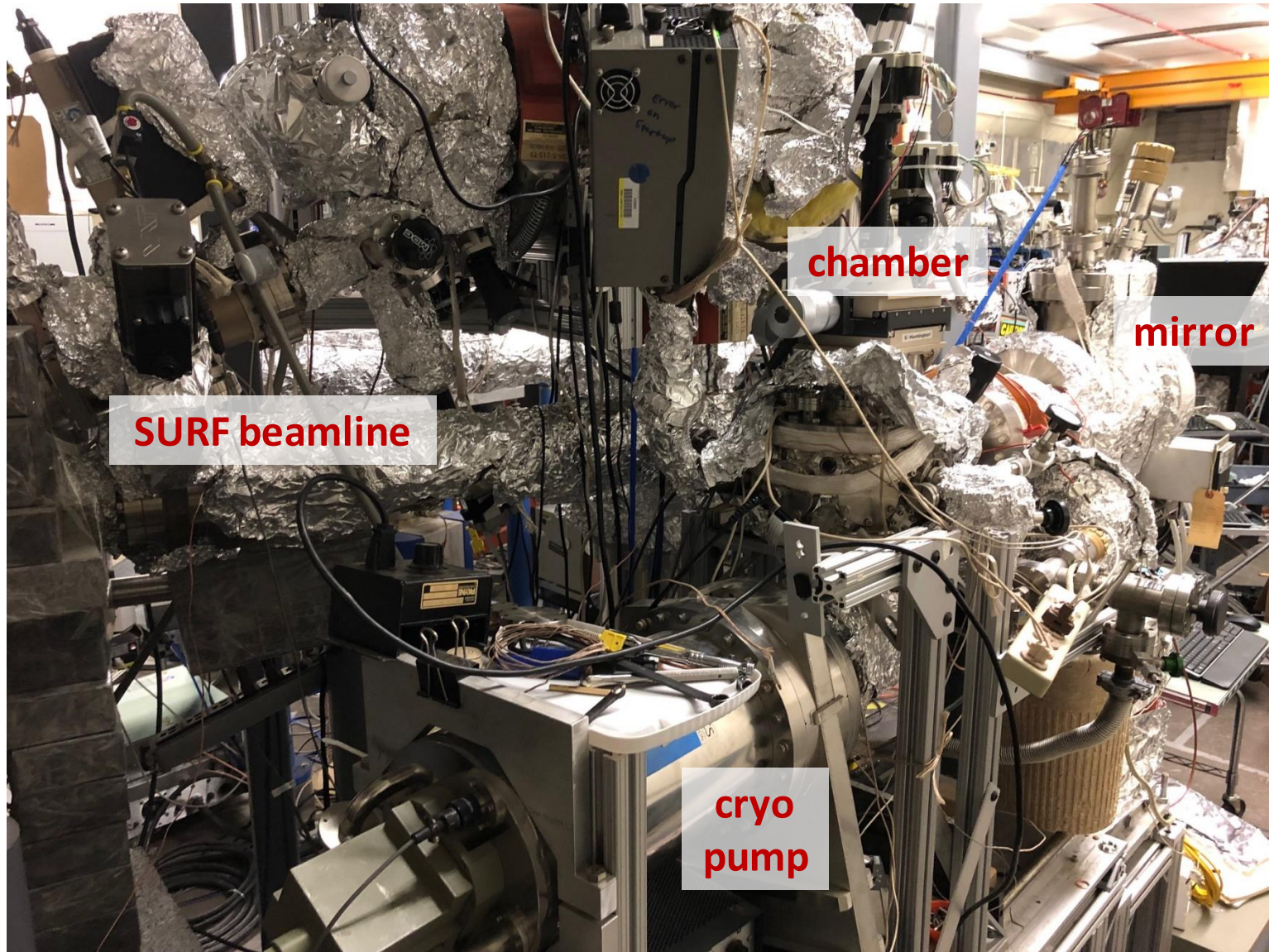
Comparing the model to the SDO degradation

SURF exposures and measurements of the oxide

SURF (synchrotron) Beamline 1a



SURF beamline 1a



SURF beamline

chamber

mirror

**cryo
pump**

SURF exposures: Knobs we can turn

	min	max	note
UV dose	40 J	3600 J	260 J/day x two weeks
average UV power	0.3 mW	3 mW	
UV cutoff	145 nm 8.6 eV	165 nm 7.5 eV	Al-Al ₂ O ₃ work function = 2.6 eV
H ₂ O pressure	10 ⁻⁸ Torr	10 ⁻⁴ Torr	minimum is chamber outgassing

SURF exposures: Measure the oxide thickness



SURF beamline 7

Transmission of EUV ($\lambda = 34 \text{ nm}$) is attenuated by oxygen.

Reproducibility $\approx \pm 10\%$

Reproducibility compares spots exposed on different filters with the same pressure and dose.

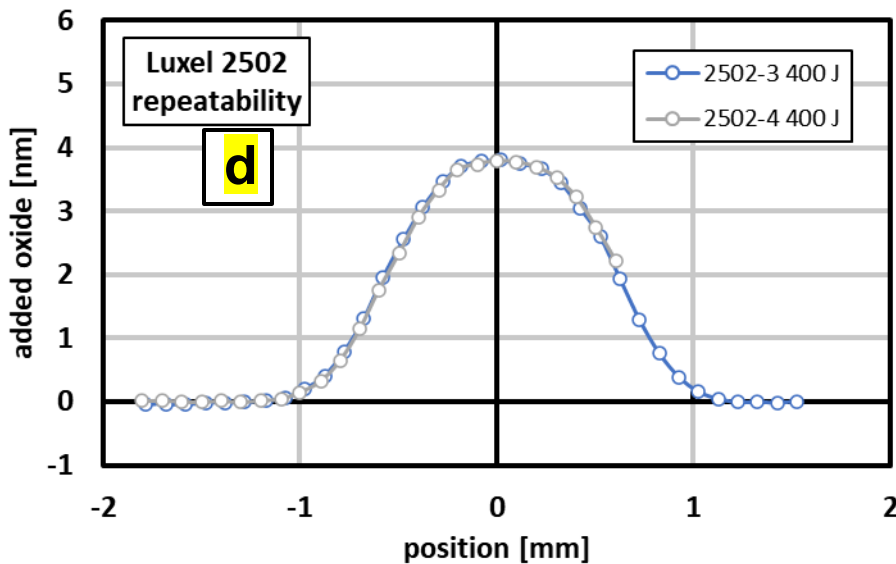
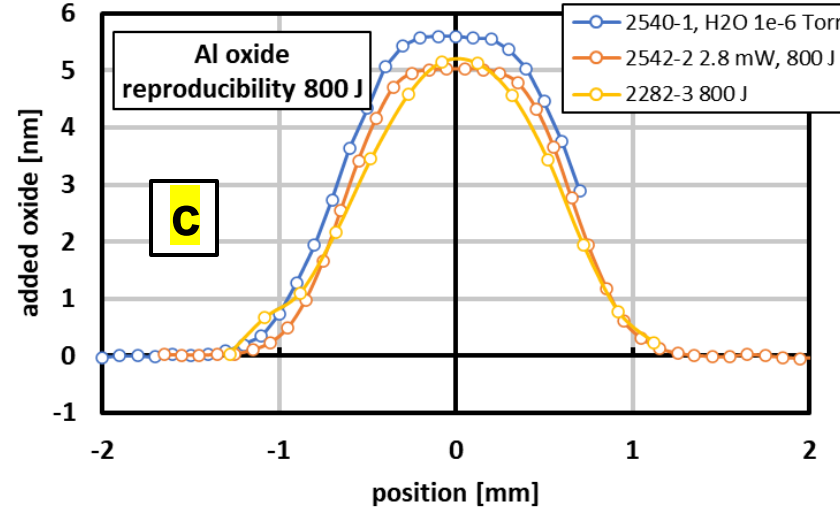
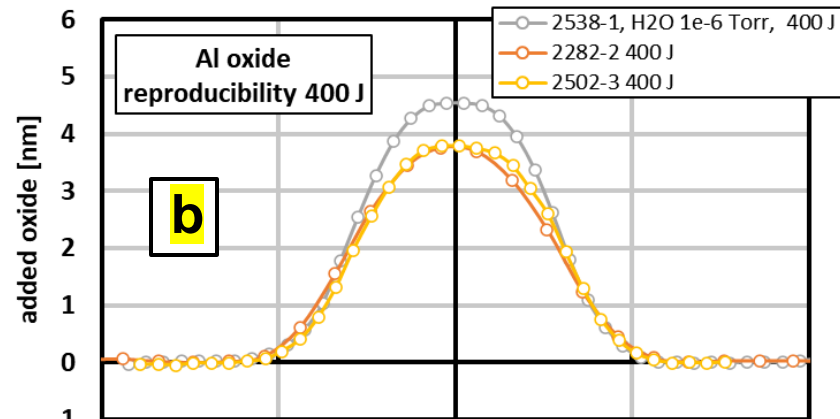
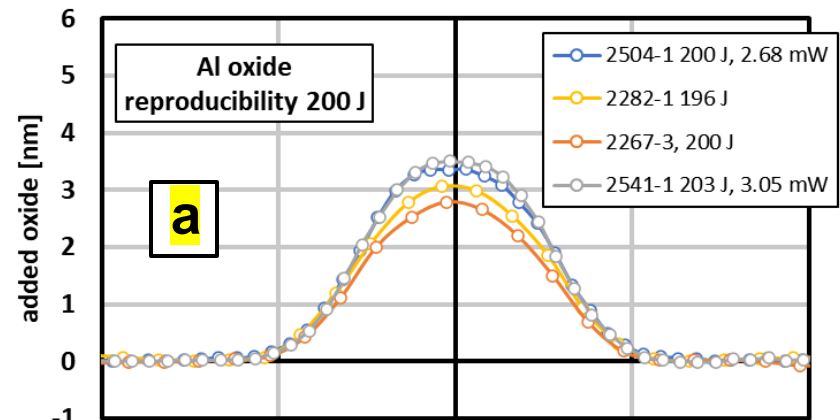
Repeatability compares spots on the same filter.

a: Peak reproduced to about $\pm 10\%$.

b: Peak reproduced to about $\pm 10\%$.

c: Shape as well as the amplitude can vary.

d: Repeatability is about $\pm 1\%$.

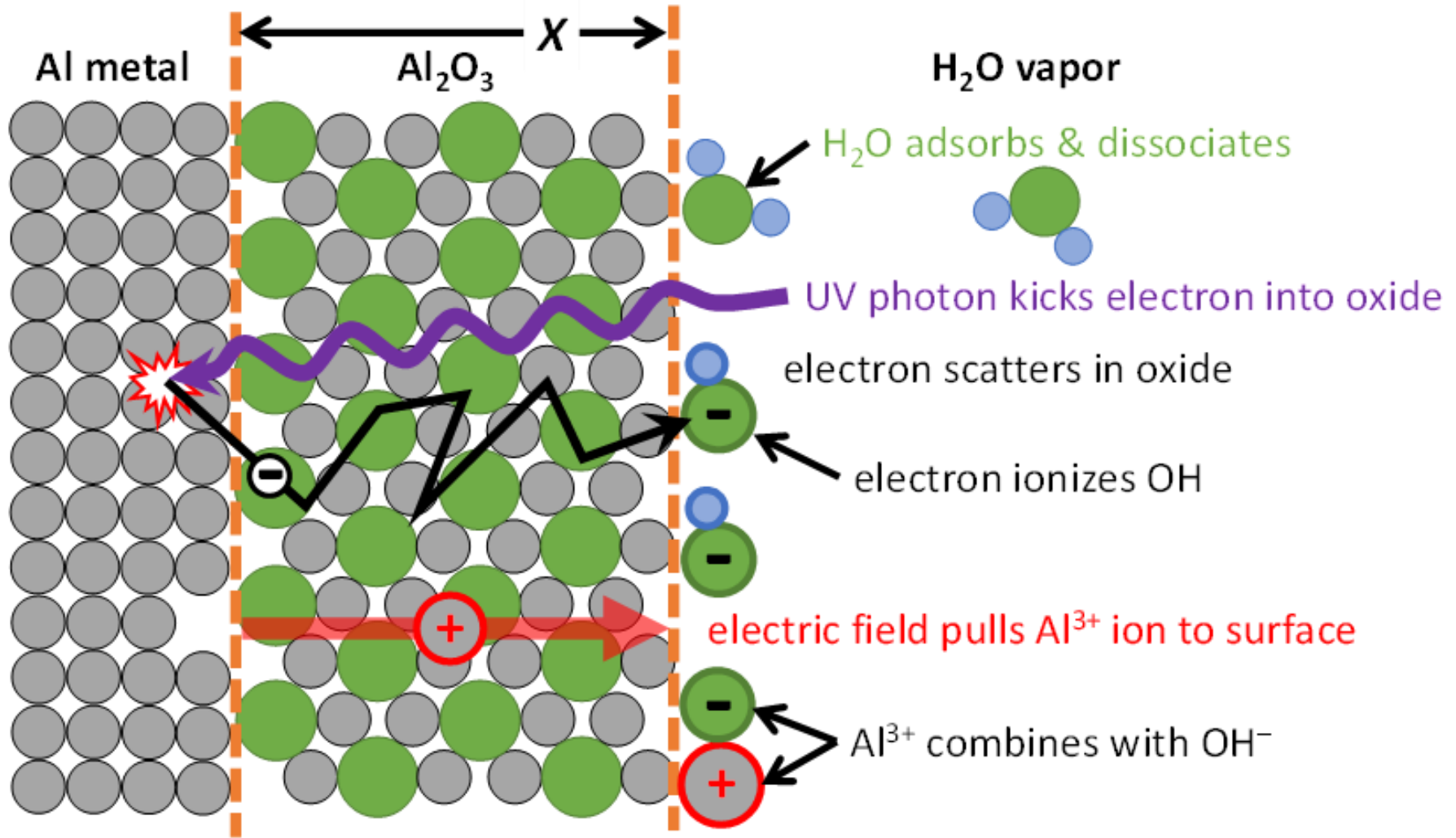


Modeling the oxide growth

The five stages of UV-induced oxidation

1. UV photons kicks electrons from the metal into the oxide.
2. The electrons scatter in the oxide. Some reach the oxide-vacuum surface.
3. Electrons at the surface react with adsorbed H_2O to create OH^- ions.
4. The OH^- ions create a field that pulls Al^{+3} ions to the oxide-vacuum surface.
5. The Al^{+3} and OH^- ions combine and create Al_2O_3 .

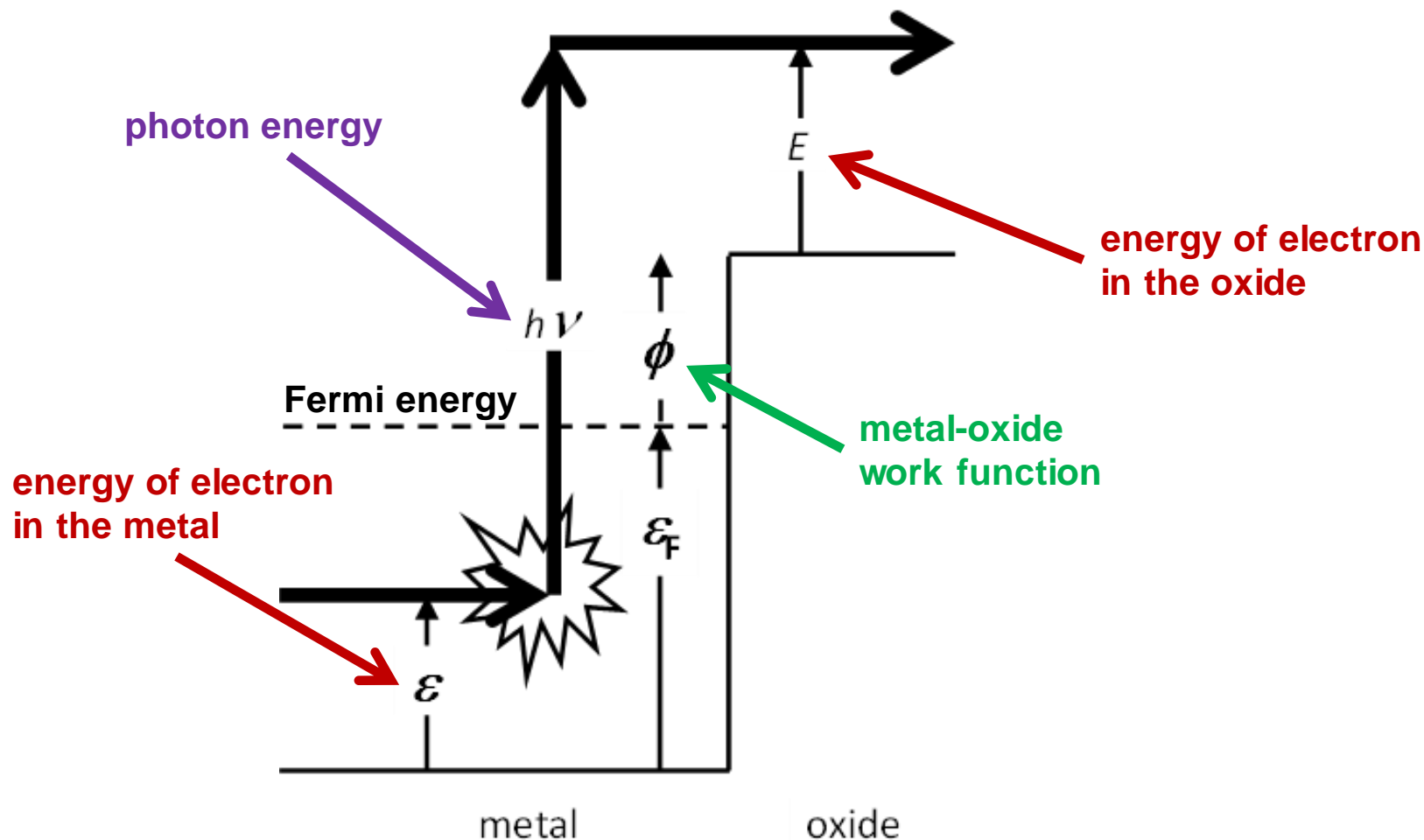
Concepts in the model



The five stages of UV-induced oxidation

1. **UV photons kicks electrons from the metal into the oxide.**
2. The electrons scatter in the oxide. Some reach the oxide-vacuum surface.
3. Electrons at the surface react with adsorbed H_2O to create OH^- ions.
4. The OH^- ions create a field that pulls Al^{+3} ions to the oxide-vacuum surface.
5. The Al^{+3} and OH^- ions combine and create Al_2O_3 .

Excitation and emission of electron into the oxide

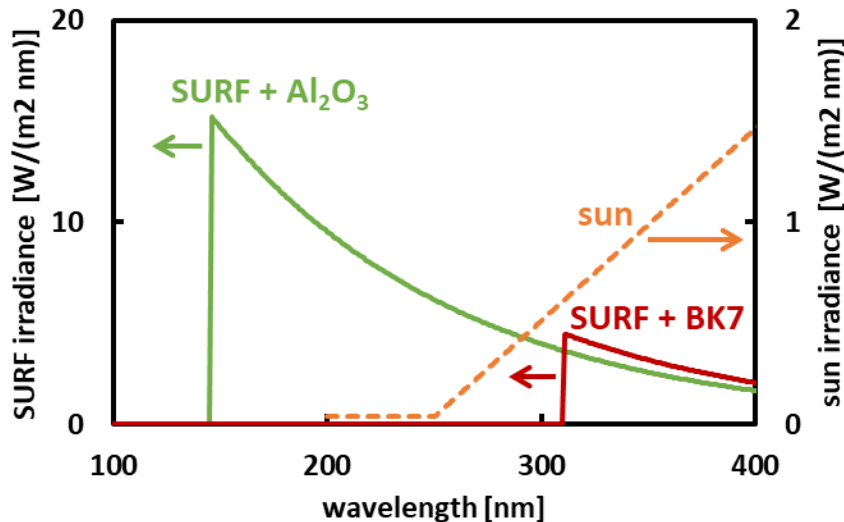


Excitation and emission of electron into the oxide

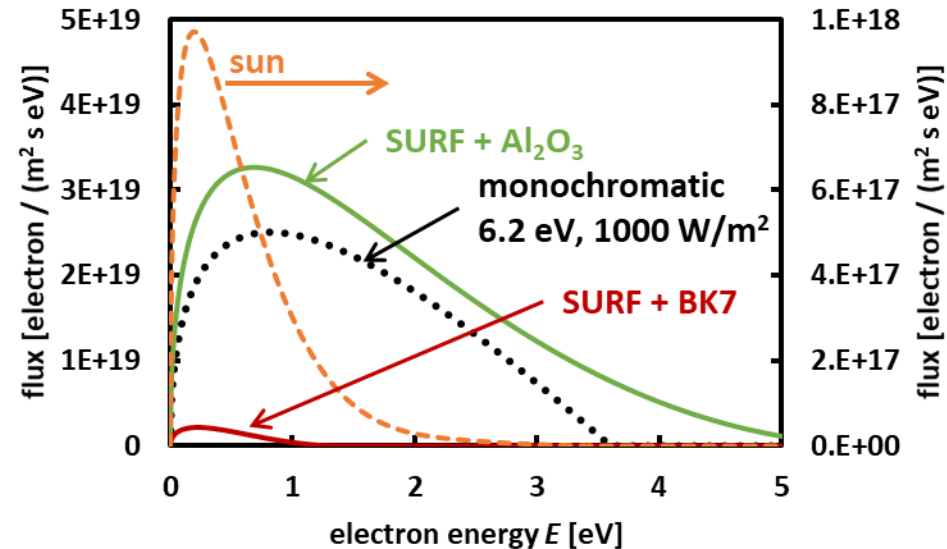
UV source	UV intensity $I_0(0)$ [J m ⁻² s ⁻¹]	electron flux J_{e0} [electron m ⁻² s ⁻¹]	mean energy $\langle E \rangle$ [eV]
sun	2.55×10^2	8.1×10^{17}	0.59
SURF SiO ₂	1.55×10^4	6.5×10^{19}	1.40
SURF Al ₂ O ₃	1.51×10^4	8.5×10^{19}	1.66
$h\nu = 6.2$ eV	1.00×10^3	5.9×10^{19}	1.41

The injected electrons have a broad distribution of energies.

photons



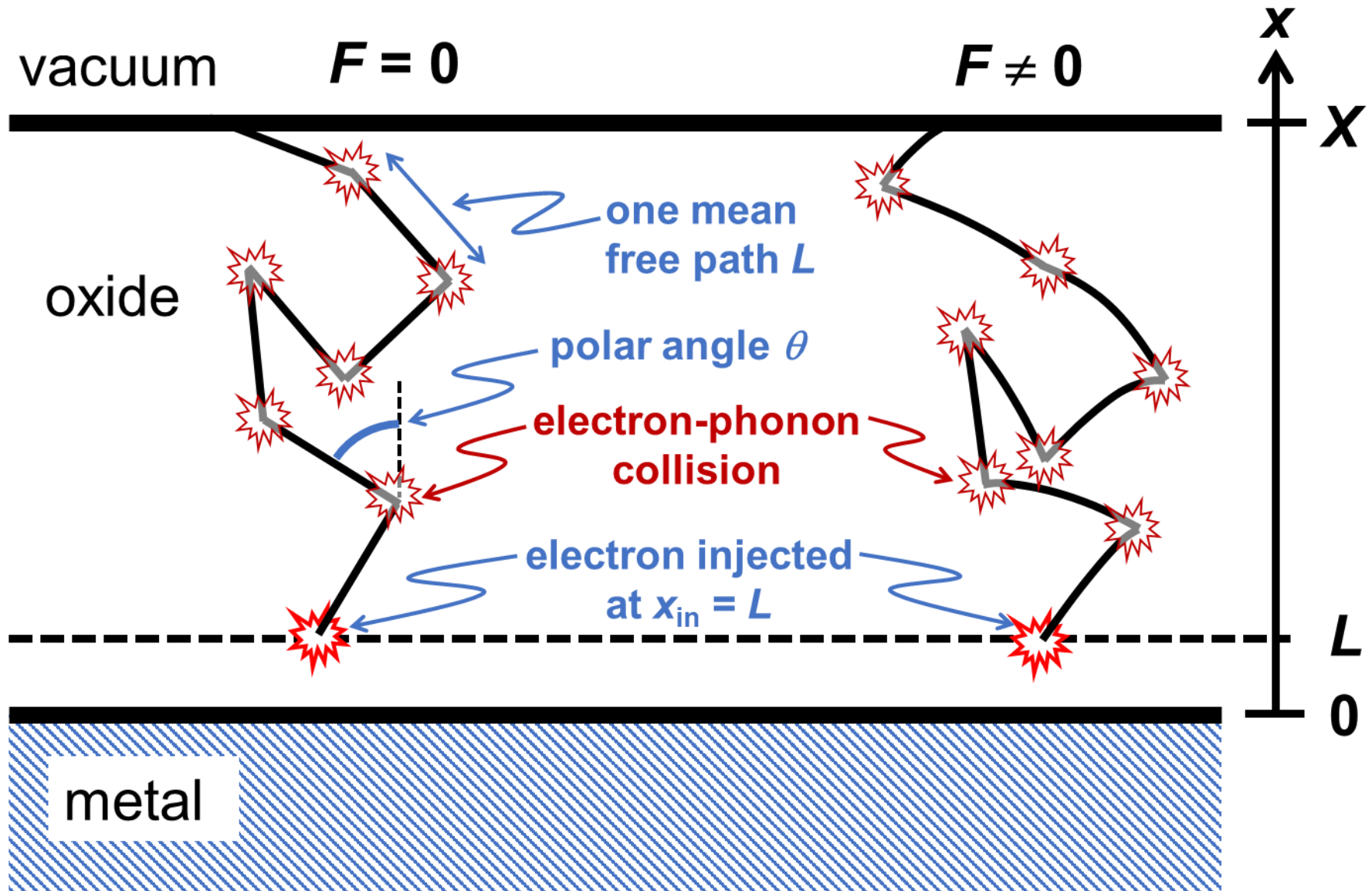
electrons



The five stages of UV-induced oxidation

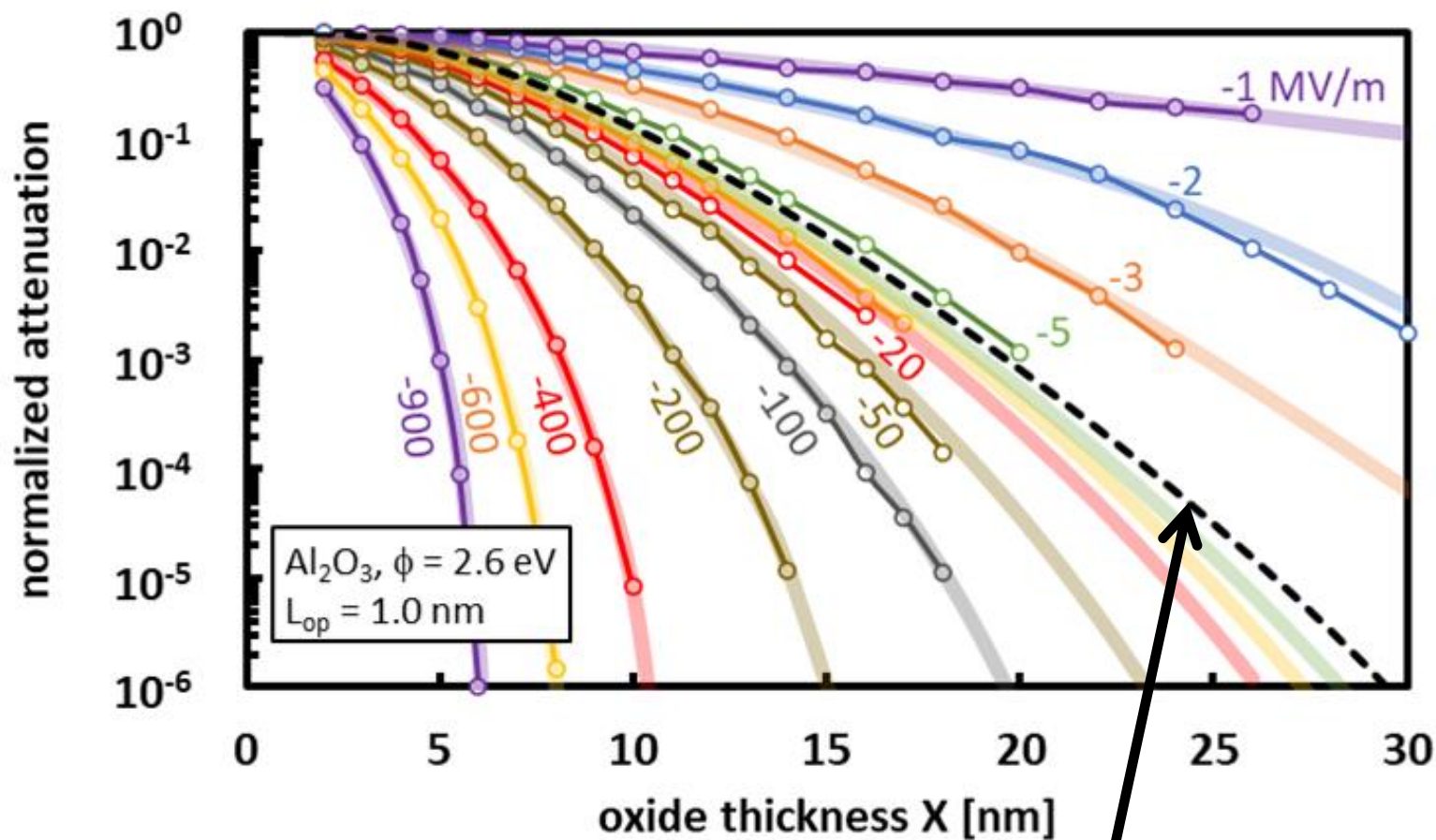
1. UV photons kicks electrons from the metal into the oxide.
- 2. The electrons scatter in the oxide. Some reach the oxide-vacuum surface.**
3. Electrons at the surface react with adsorbed H_2O to create OH^- ions.
4. The OH^- ions create a field that pulls Al^{+3} ions to the oxide-vacuum surface.
5. The Al^{+3} and OH^- ions combine and create Al_2O_3 .

Electron scattering in the oxide



metal

Electron scattering in the oxide: 2D Monte Carlo

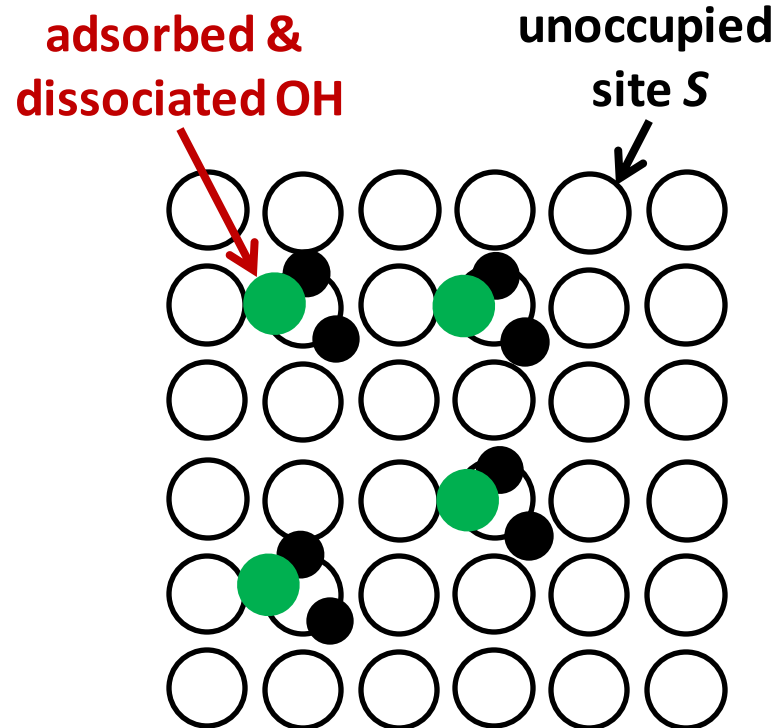
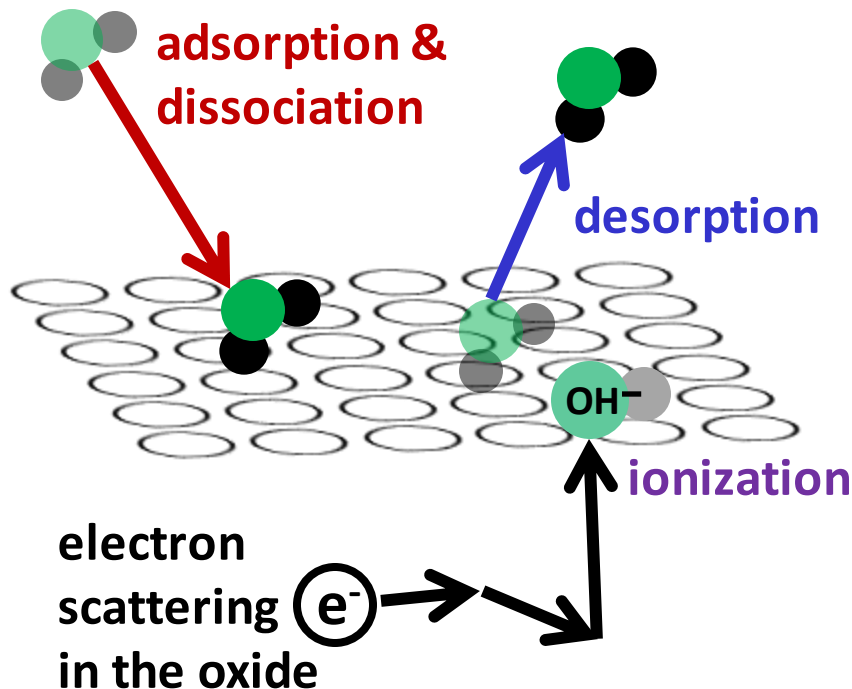
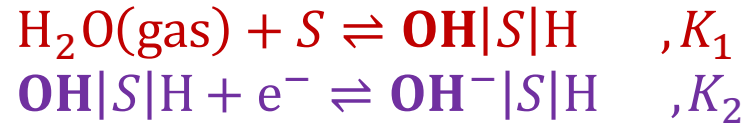


The five stages of UV-induced oxidation

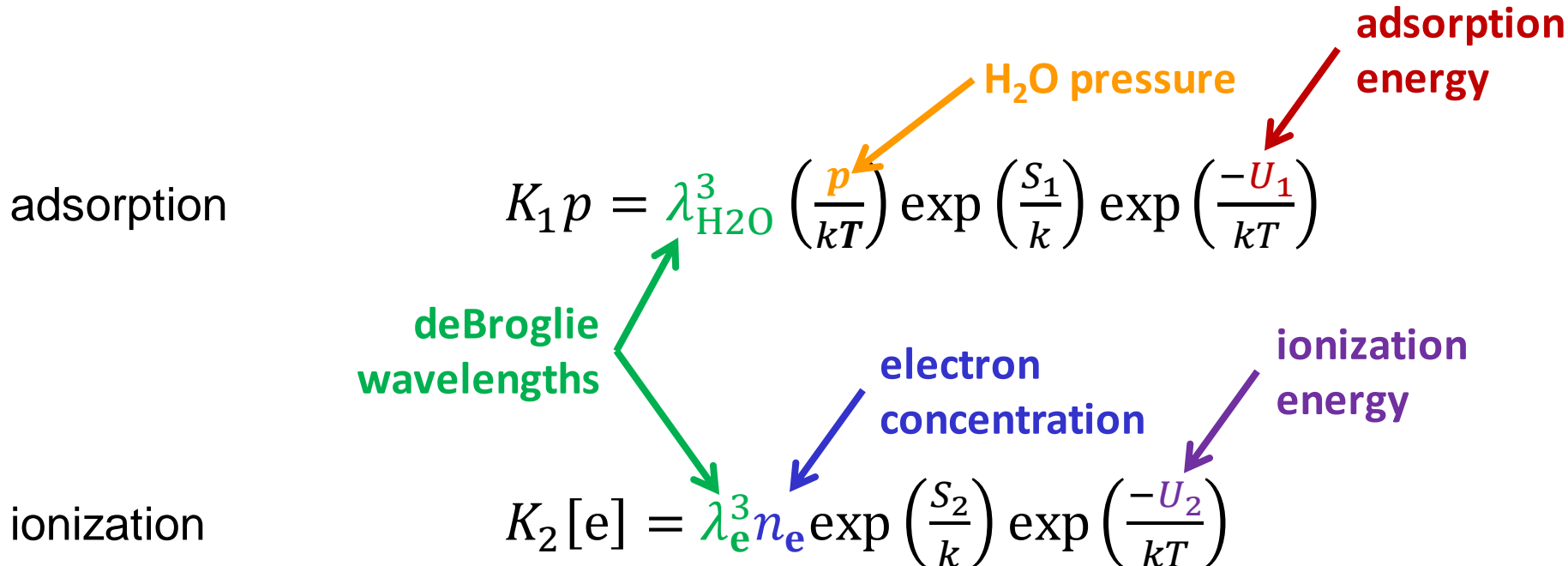
1. UV photons kicks electrons from the metal into the oxide.
2. The electrons scatter in the oxide. Some reach the oxide-vacuum surface.
- 3. Electrons at the surface react with adsorbed H_2O to create OH^- ions.**
4. The OH^- ions create a field that pulls Al^{+3} ions to the oxide-vacuum surface.
5. The Al^{+3} and OH^- ions combine and create Al_2O_3 .

Surface reactions: adsorption, then ionization

adsorption & dissociation
ionization



Surface reactions: equilibrium constants: K_1, K_2



The five stages of UV-induced oxidation

1. UV photons kicks electrons from the metal into the oxide.
2. The electrons scatter in the oxide. Some reach the oxide-vacuum surface.
3. Electrons at the surface react with adsorbed H_2O to create OH^- ions.
4. **The OH^- ions create a field that pulls Al^{+3} ions to the oxide-vacuum surface.**
5. The Al^{+3} and OH^- ions combine and create Al_2O_3 .

Transport of Al^{+3} : Oxide growth rate dX/dt

Oxide growth rate:

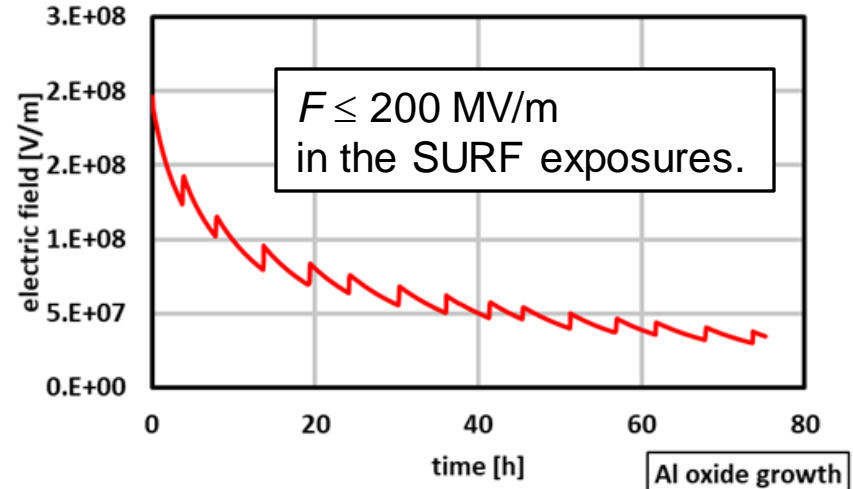
$$\frac{dX}{dt} = \Omega J$$

volume of a unit Al_2O_3 ion flux

Electric field:

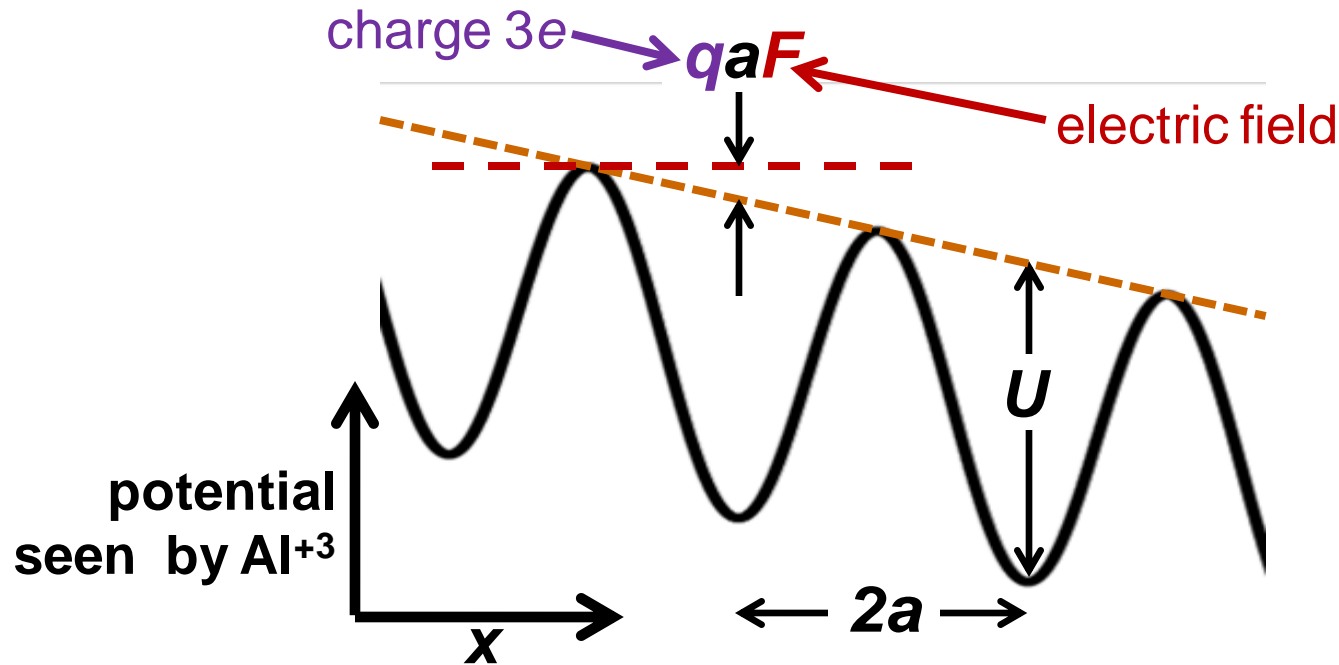
$$F = \frac{e\sigma}{\epsilon}$$

surface charge density



Use transition state theory to obtain the ion flux in terms of the electric field F .

Transport of Al^{3+} : Transition state theory



If the flux is uniform ($\partial J/\partial x = 0$) and the field is uniform ($\partial F/\partial x = 0$), the flux is

$$J = 4a\nu \exp\left(-\frac{U}{kT}\right) \sinh\left(\frac{qaF}{kT}\right) \left[n - \frac{kT}{qF} \frac{dn}{dx} \right]$$

attempt frequency $\sim kT/h$

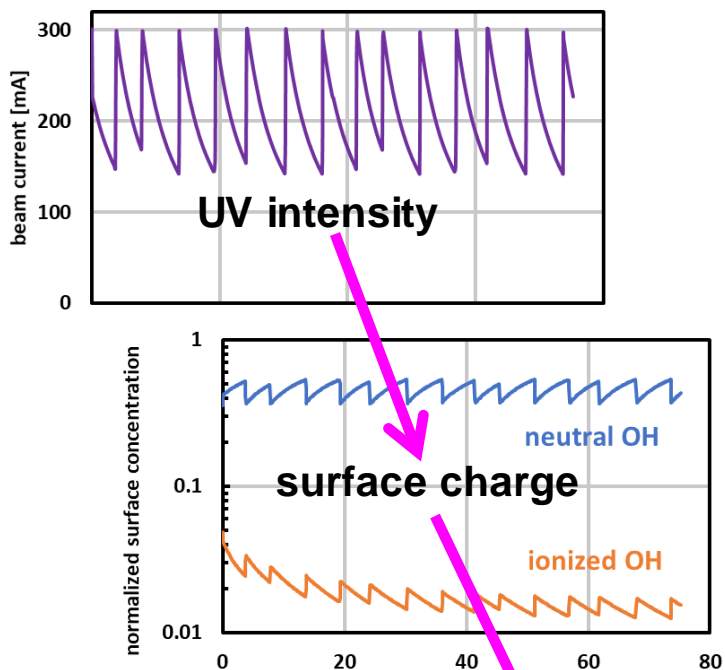
density of mobile ions

The five stages of UV-induced oxidation

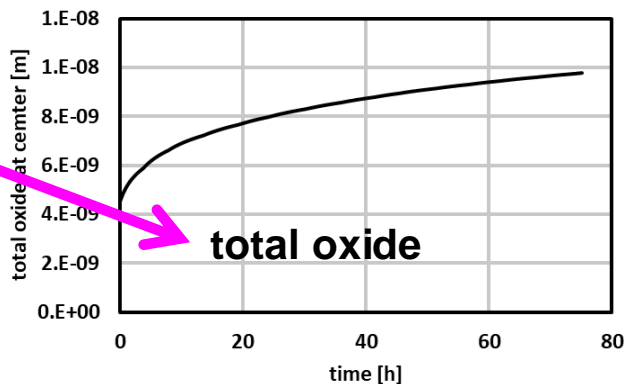
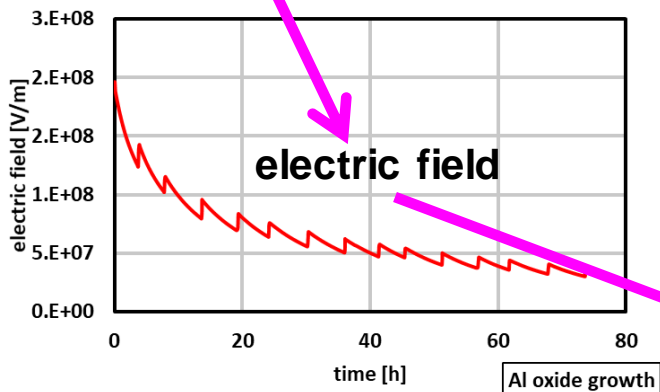
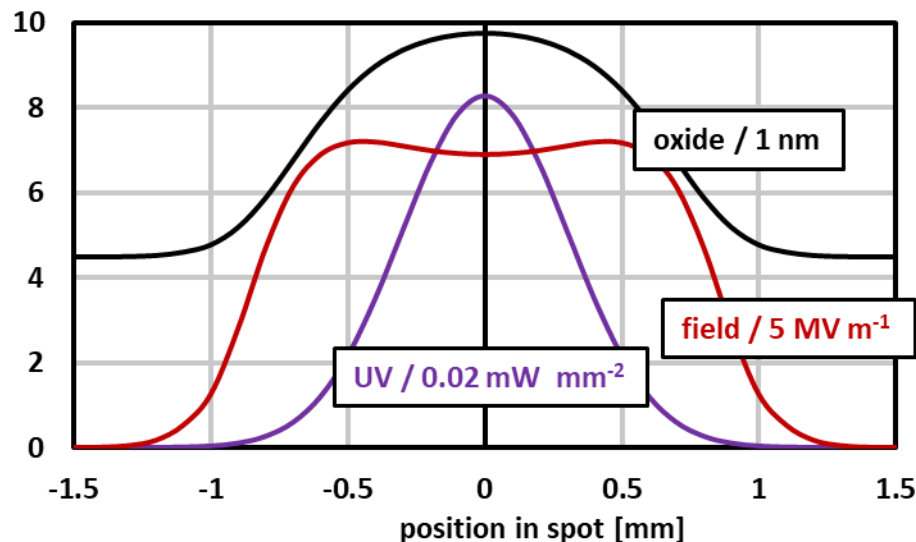
1. UV photons kicks electrons from the metal into the oxide.
2. The electrons scatter in the oxide. Some reach the oxide-vacuum surface.
3. Electrons at the surface react with adsorbed H_2O to create OH^- ions.
4. The OH^- ions create a field that pulls Al^{+3} ions to the oxide-vacuum surface.
5. **The Al^{+3} and OH^- ions combine and create Al_2O_3 .**

Luxel 2282-3: Evolution of charge, field, oxide

History at spot center



Distributions at end of run



Comparing the model to the oxide measurements

Modeling strategy

1. Decide what goes in the model.

2. Fit all the SURF exposures by one set of free parameters.

electron mean free path	L
ion barrier hop energy	U_0
H ₂ O adsorption energy	U_1
OH ⁻ ionization energy	U_2
H ₂ O/photon desorption yield	Y

3. Use literature values of well-known parameters.

Initial oxide thickness	X_0
Energy of an optical phonon	E_{phonon}
Al-Al ₂ O ₃ work function	ϕ

4. Modify the model's assumptions if there is a problem.

An exposure spot is not well described by the model.
A free parameter has an unphysical value.

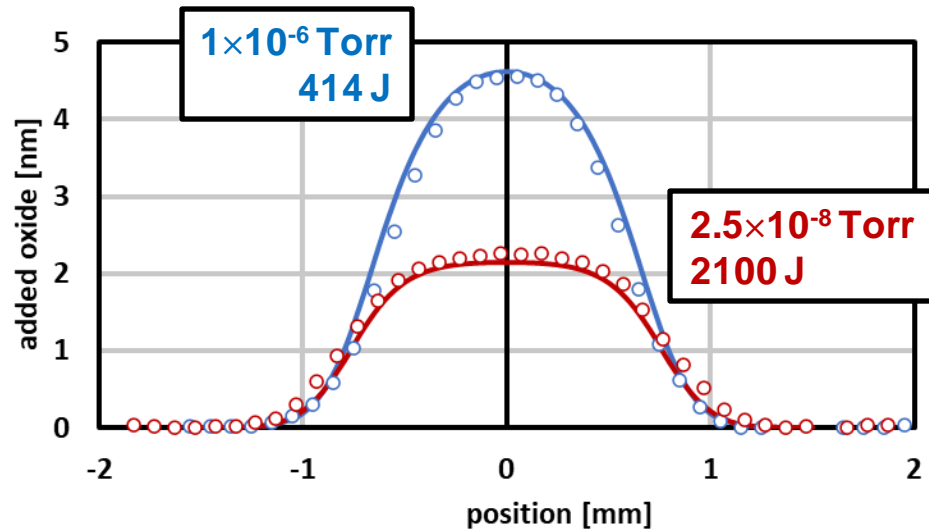
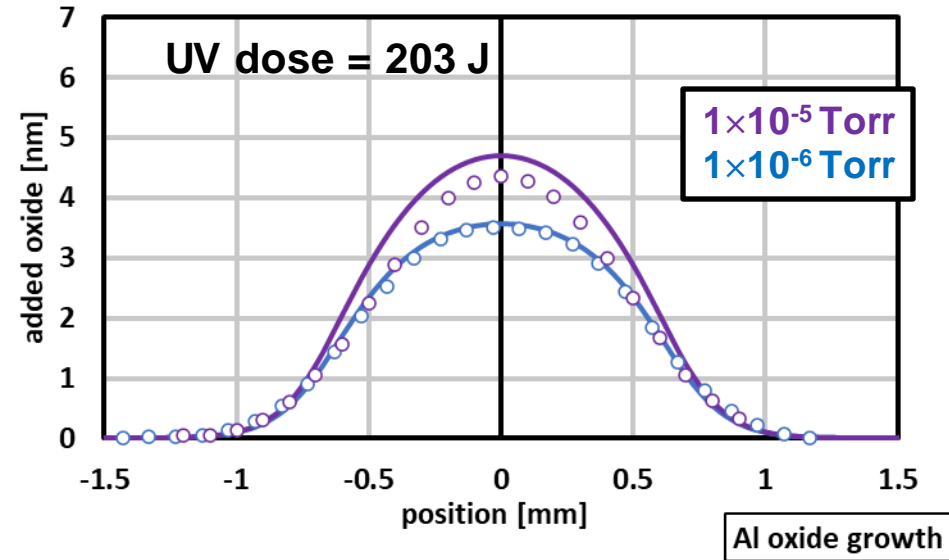
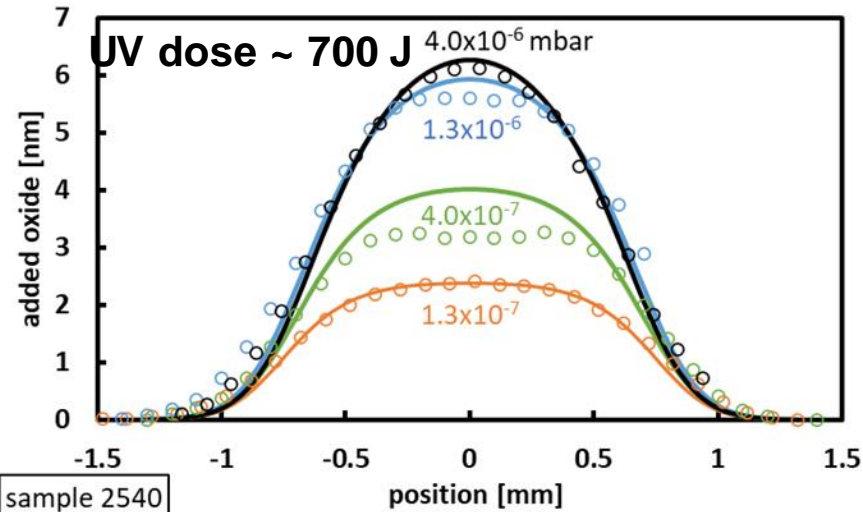
5. Use the same parameters to describe the SDO degradation.

The H₂O pressure is a free parameter.

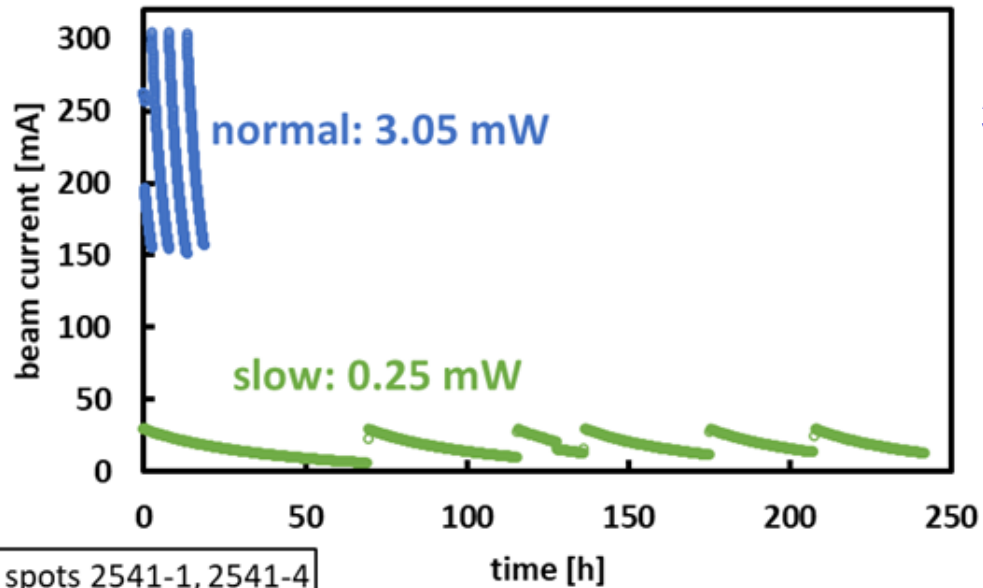


If there is
a problem

Vary the H₂O pressure

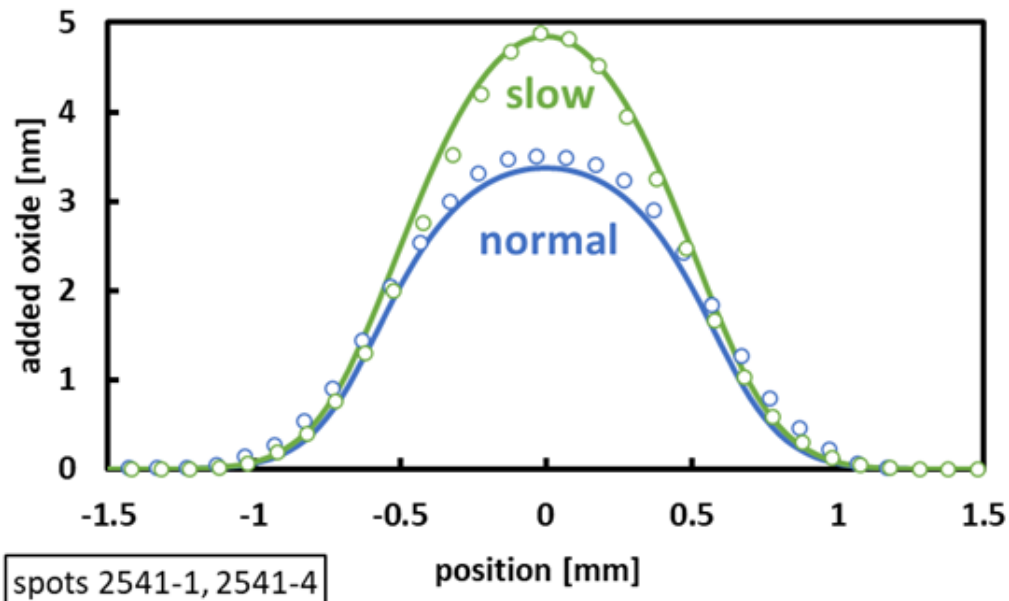


Vary the UV intensity

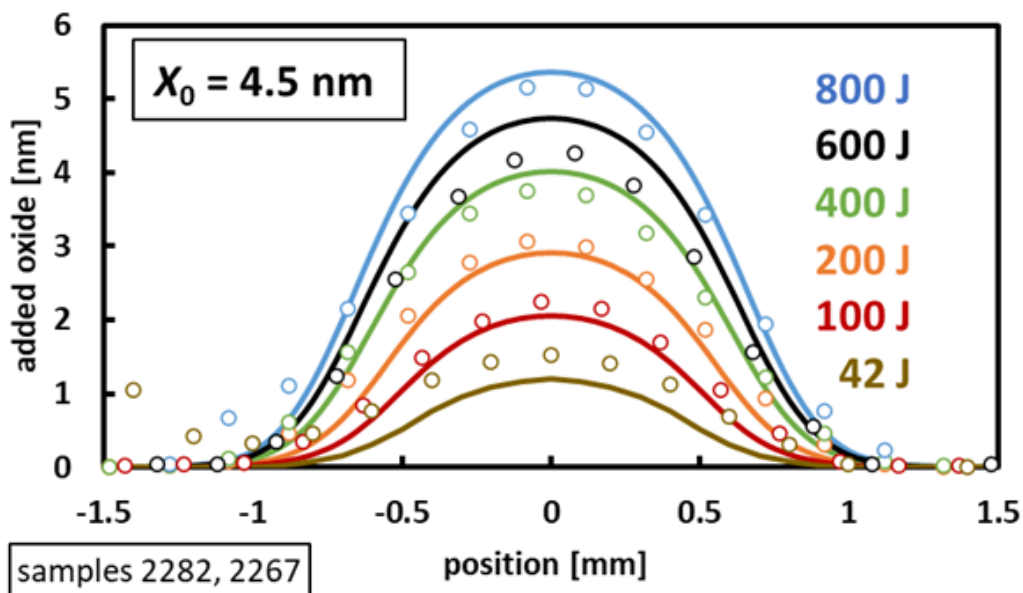
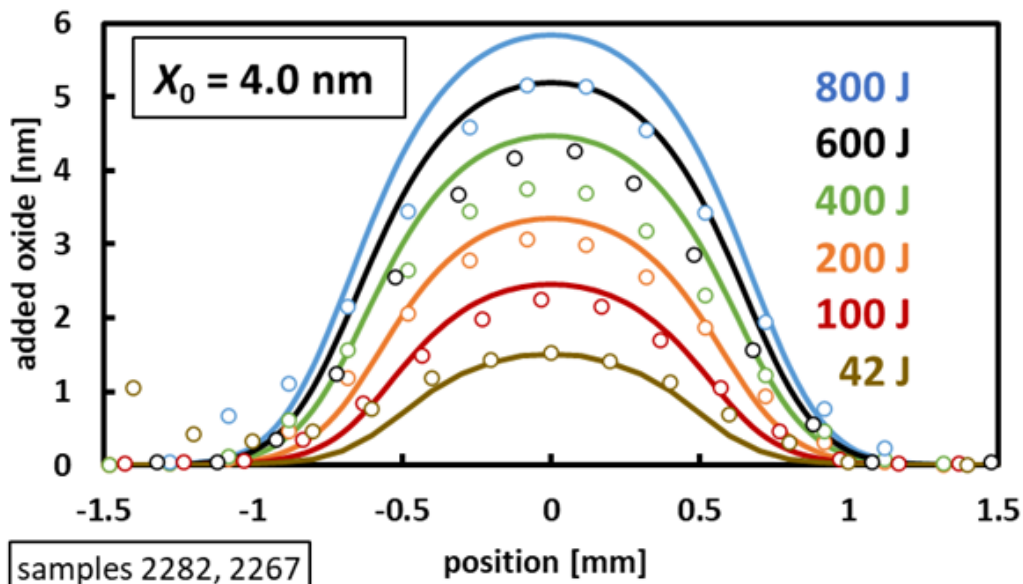


3.05 mW = 203 J / 0.8 day
 1×10^{-6} Torr H₂O

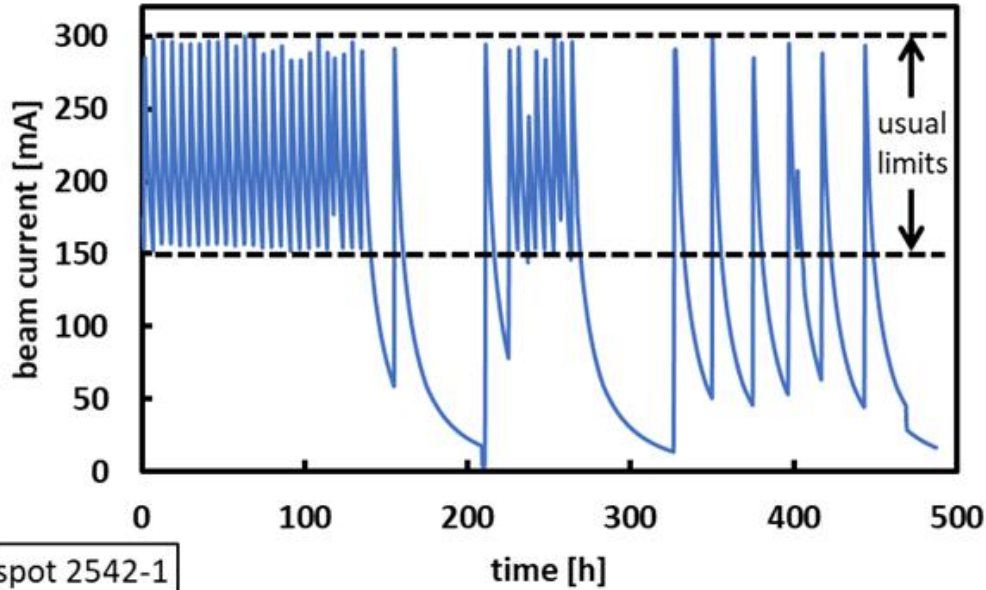
0.25 mW = 222 J / 10.1 days
 1×10^{-6} Torr H₂O



Vary the UV dose

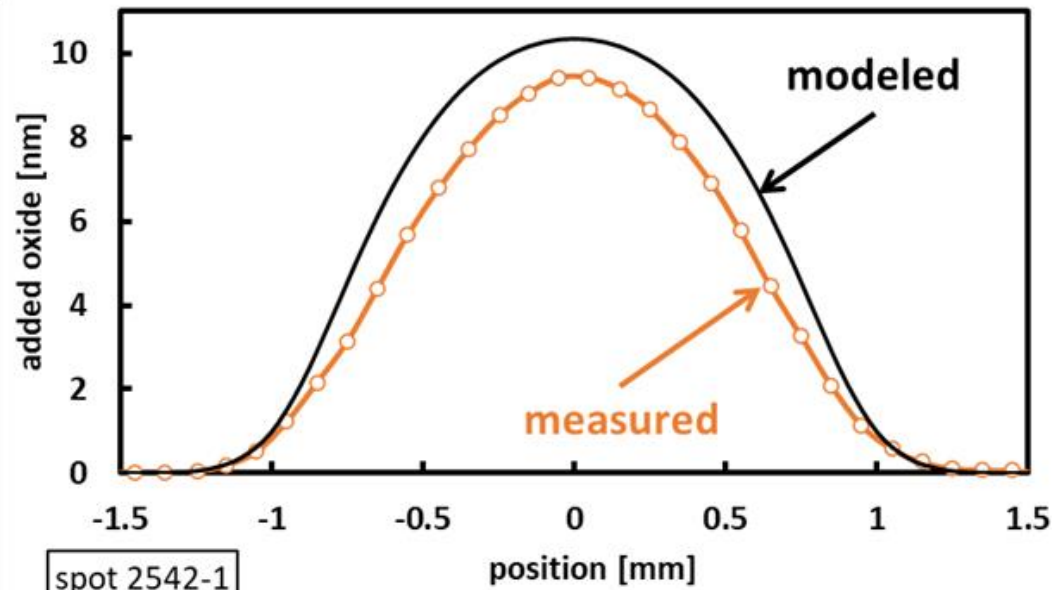


20-day exposure



Mixture of normal and slow runs

2×10^{-6} Torr H₂O



Model parameters

quantity fixed		value used	expected	why expected
initial oxide thickness	X_0	4.0 nm or 4.5 nm	(4 ± 1) nm	XPS and XRR of multiple surfaces
Al-Al ₂ O ₃ work function	ϕ	2.6 eV	(2.6 ± 0.6) eV	middle value of literature range
electron-phonon collision loss	E_{op}	0.05 eV	(0.05 ± 0.01) eV	neutron scattering

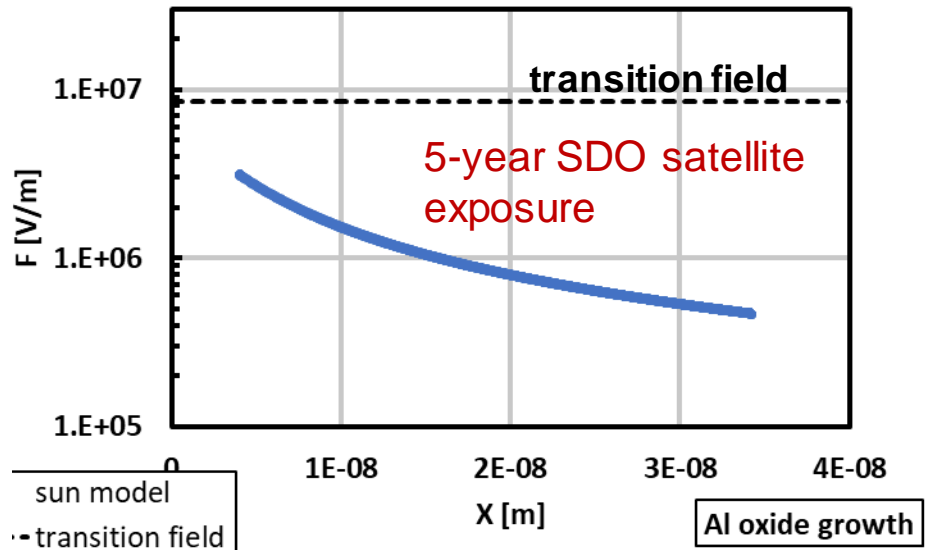
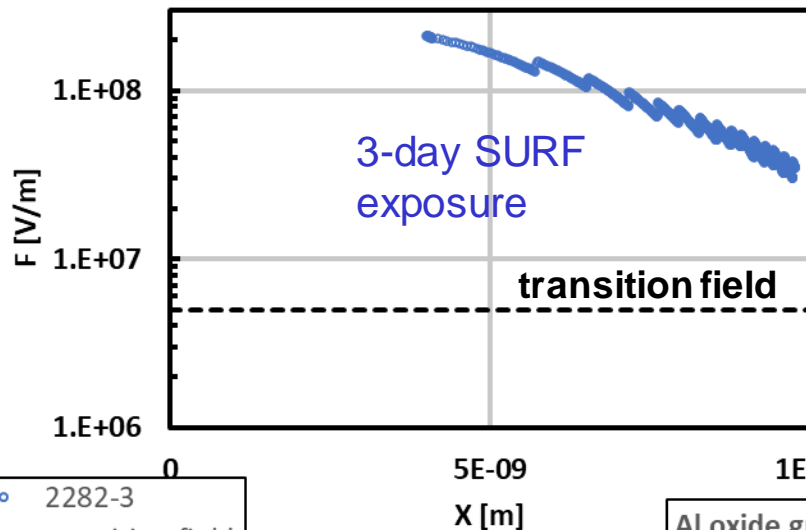
quantity fitted		value fitted	expected	why expected
electron mean free path	L	(1.22 ± 0.02) nm	(1.0 ± 0.2) nm	photoyield of biased Al-Al ₂ O ₃ -Au sandwich
ion-hop barrier energy	$+U_0$	(1.07 ± 0.02) eV	0.8 eV to 1.6 eV	oxidation at higher T by exposure to O ₂
H ₂ O adsorption energy	$-U_1$	$(1.01_{-0.02}^{+0.04})$ eV	0.5 eV to 1.8 eV	adsorption on crystal Al ₂ O ₃
OH ionization energy	$-U_2$	(0.68 ± 0.02) eV	< 1.4 eV	OH electron affinity – H ₂ O dissociation energy
H ₂ O / photon desorption yield	Y	$(4 \pm 1) \times 10^{-4}$	< 18×10^{-4}	desorption from bulk H ₂ O

What happens to a thermalized electron?

The electric field across the oxide adds a bias to the random walk of a thermalized electron. A strong electric field displaces a thermalized electron between scattering events by more than the mean free path L . The electron is ultimately swept back to the metal.

$$F \gg \frac{kT}{eL} = \frac{(0.026 \text{ eV})}{(1 \text{ nm})} = 26 \text{ MV/m}$$

	<u>oxide</u>	<u>electric field</u>	<u>electron fate</u>
Luxel 2282-3, start	4 nm	211 MV/m	Swept back to metal
Luxel 2282-3, end (75 h)	10 nm	35 MV/m	Swept back to metal
SDO, start	4 nm	3.1 MV/m	Reaches oxide-vacuum surface
SDO, end (5 years)	29 nm	0.5 MV/m	Reaches oxide-vacuum surface



Comparing the model to the SDO degradation

Three questions

1. Were the oxide growth rates in the laboratory consistent with those on SDO?
2. Was the water vapor pressure on SDO sufficient to produce such oxidation?
3. What was the source of the water vapor on SDO?

SDO and laboratory conditions

	SDO	laboratory
radiation spectrum	optical and near-UV	deep-UV and near-UV
H₂O pressure	$\sim 10^{-8}$ mbar	3×10^{-8} mbar to 10^{-4} mbar
exposure duration	5 years	1 hour to 20 days

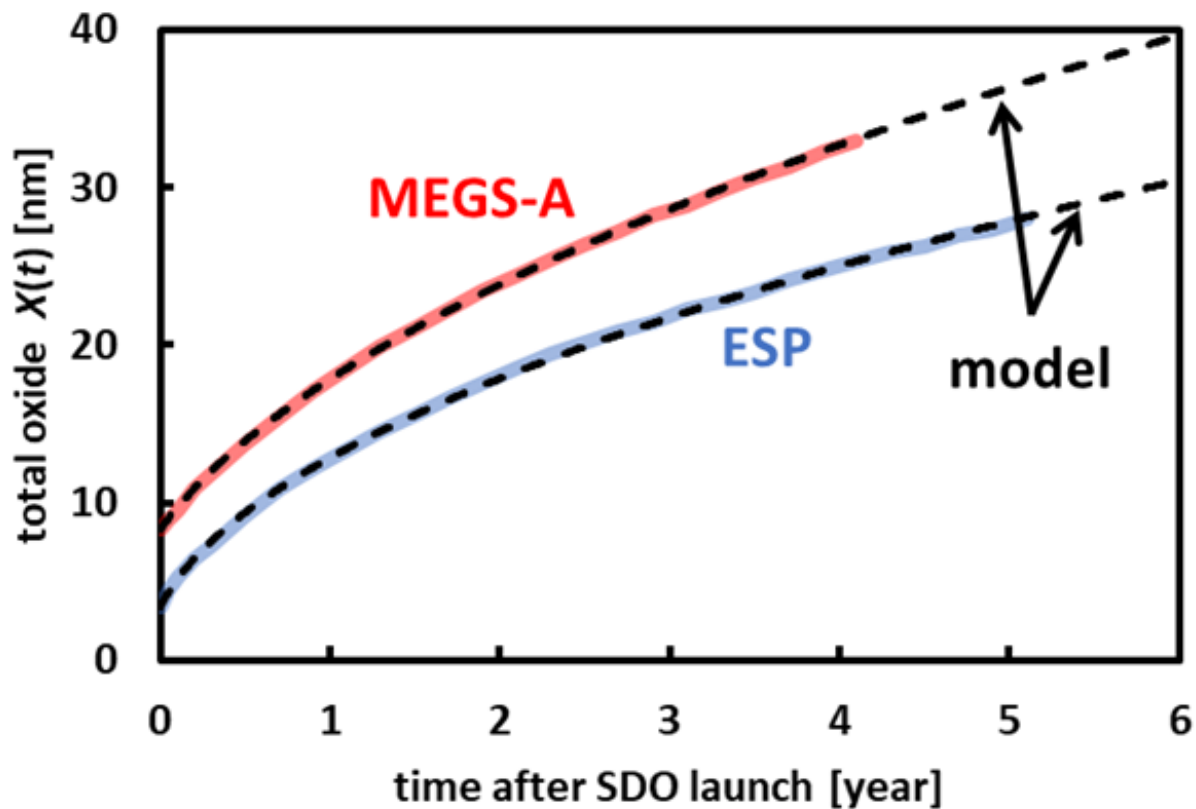
Use the same parameter values that described the SURF oxide growth, with the following exceptions:

- Modify the fixed parameters determined by the incident UV spectral intensity and the resulting photoelectron energy distribution.
- Use the initial oxide thickness X_0 found by fitting the data to the square-root description.

$$X(t) = X_0 \left(1 + \frac{t}{t_0} \right)^{1/2}$$

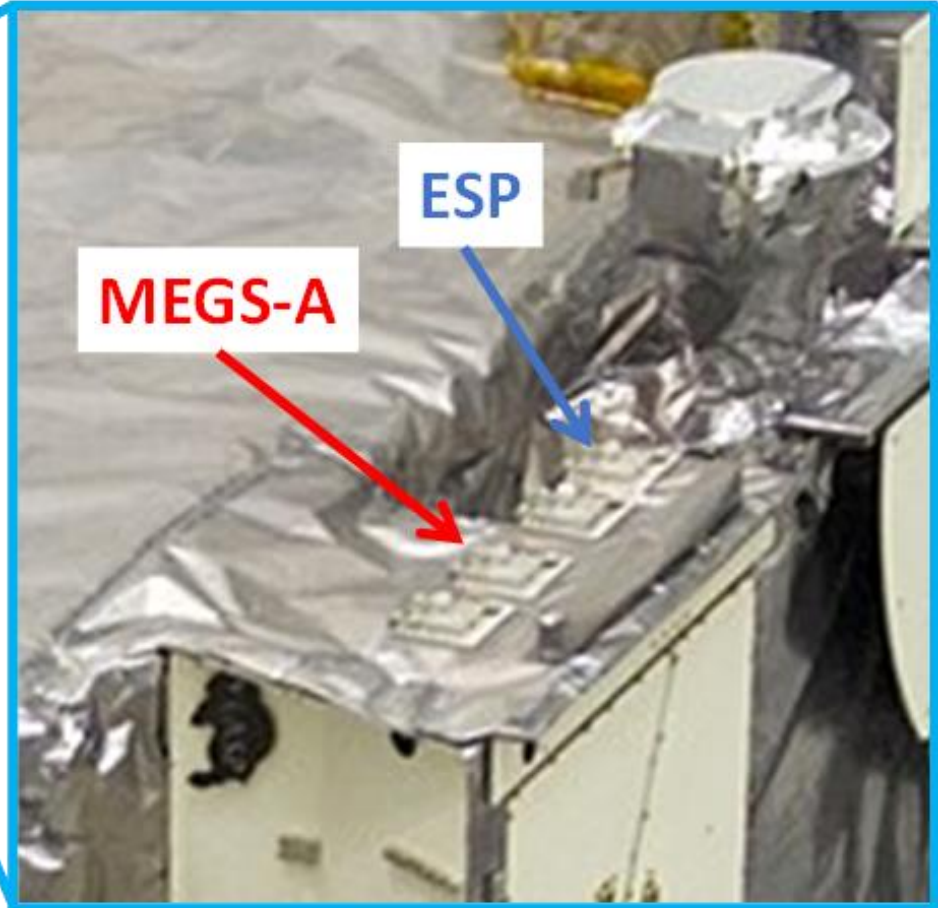
- Allow the temperature and H₂O pressure to be free parameters.

Fit results

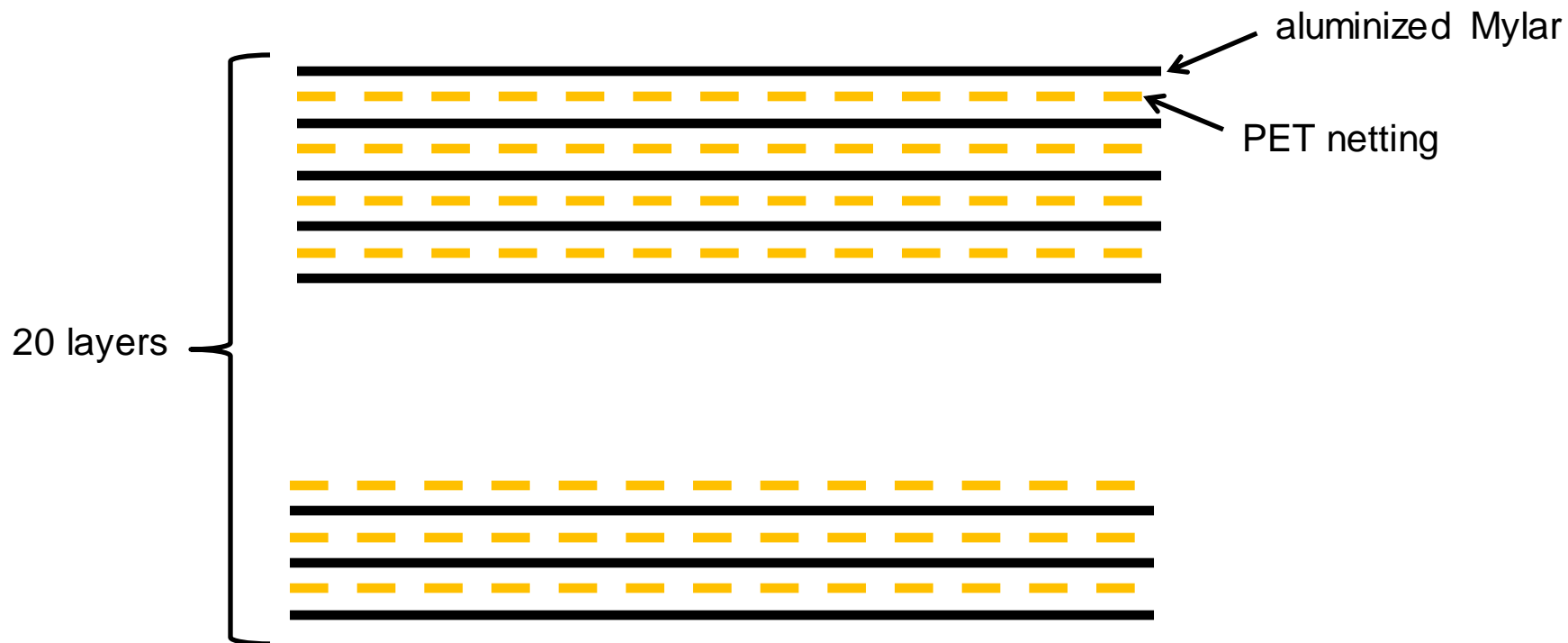


	ESP		MEGS-A	
X_0	3.4	nm	8.3	nm
t_0	0.074	year	0.277	year
T	306 ± 1	K	314 ± 1	K
$p_{\text{H}_2\text{O}}$	$(0.58 \pm 0.03) \times 10^{-8}$	mbar	$(1.5 \pm 0.10) \times 10^{-8}$	mbar

SDO shortly before launch

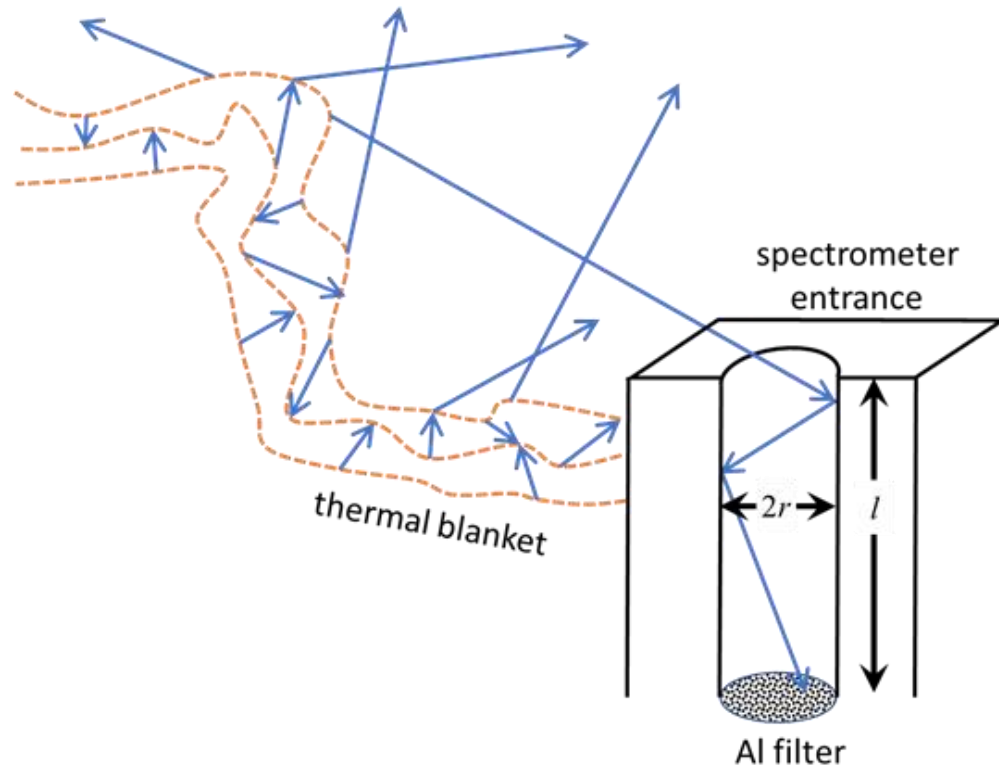


The thermal blanket



At saturation, the blanket can store $0.63 \text{ g} / \text{m}^2$.

The spectrometer can "see" the blanket emission

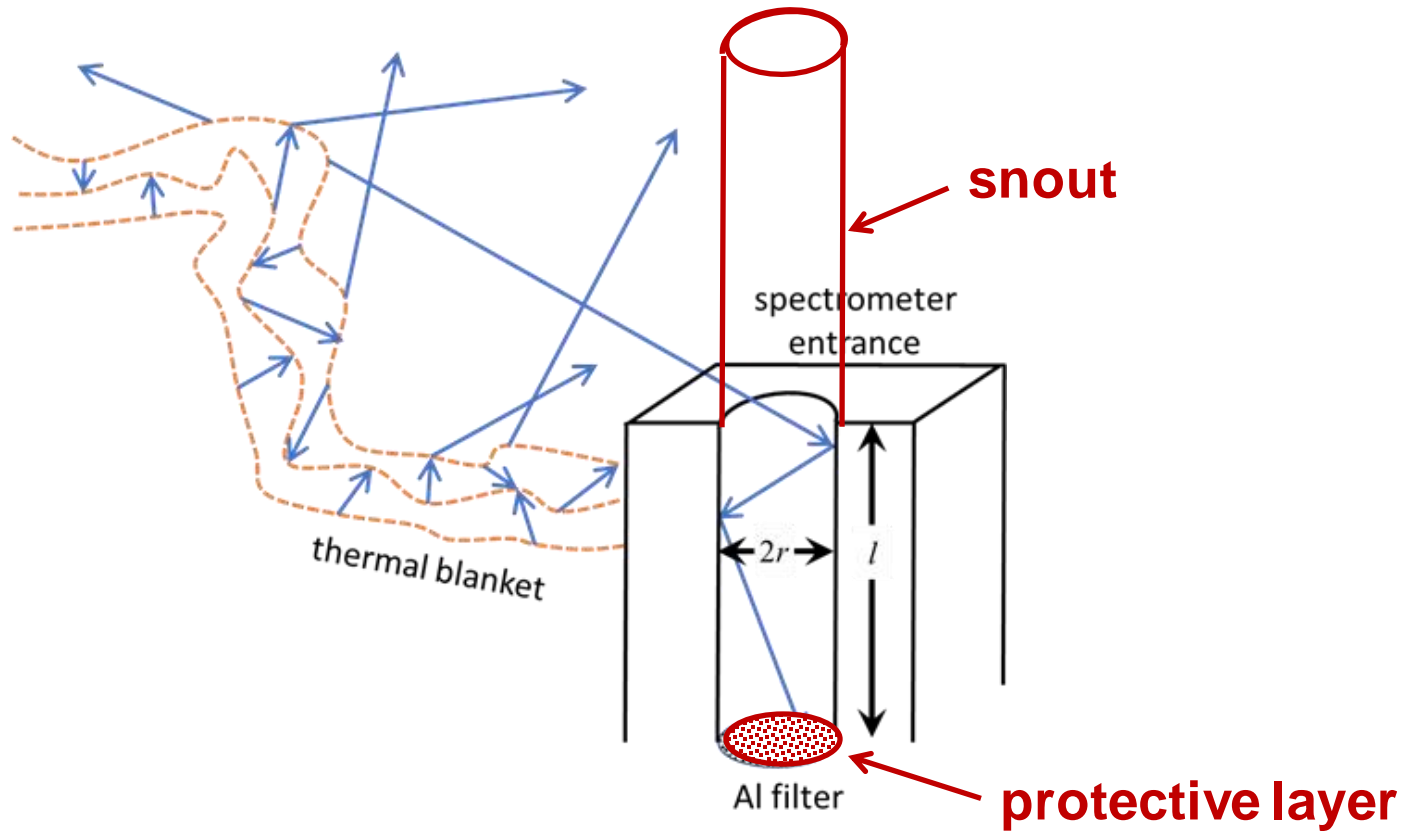


pressure at the filter = (flow out of spectrometer) / (entrance flow conductance)

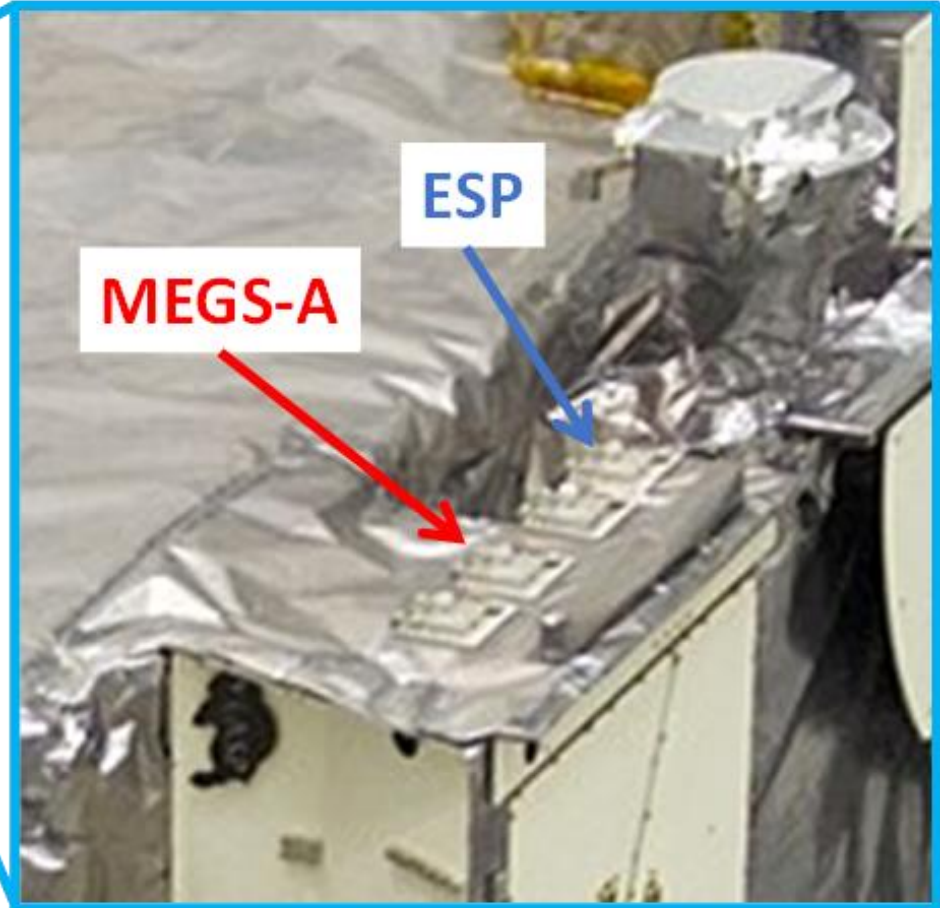
flow out of spectrometer = flow into spectrometer

If 10% of the entrance view is the blanket, then
water released in 5 years from blanket was $0.4 \text{ g} / \text{m}^2$.

Possible improvements



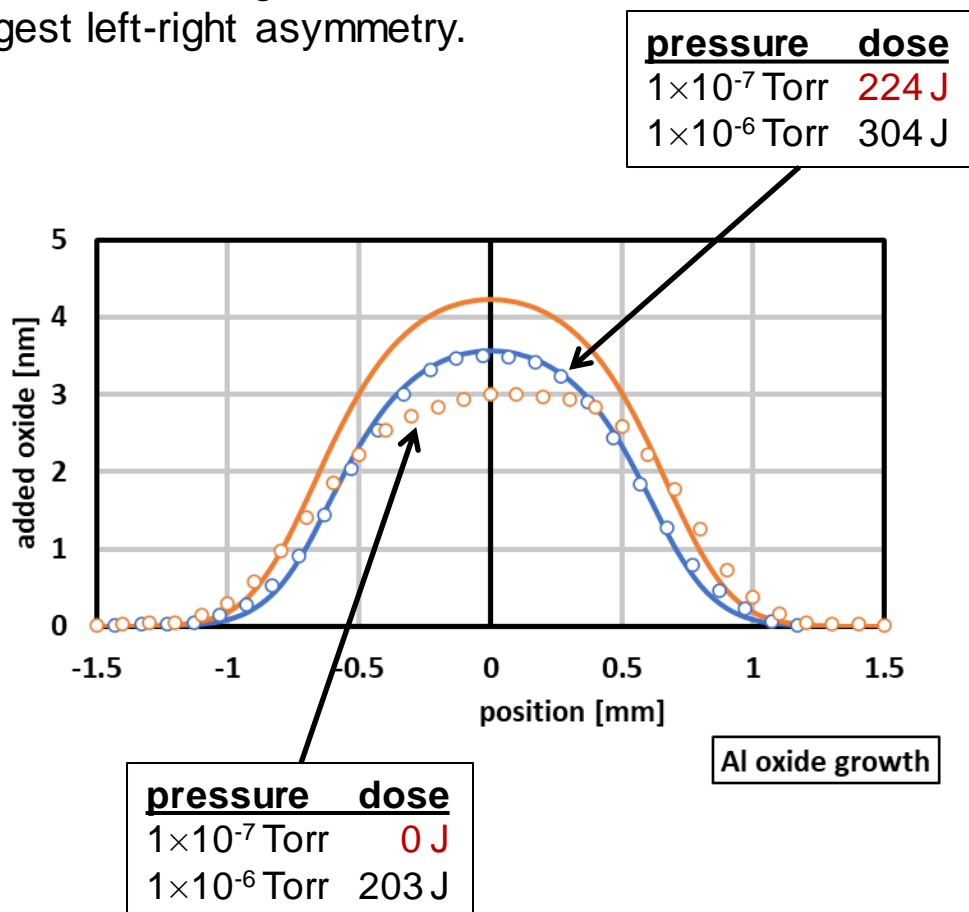
SDO shortly before launch



Supplements

2541-3: pressure sequence

- The model overpredicts the oxide growth.
- This spot has the largest left-right asymmetry.

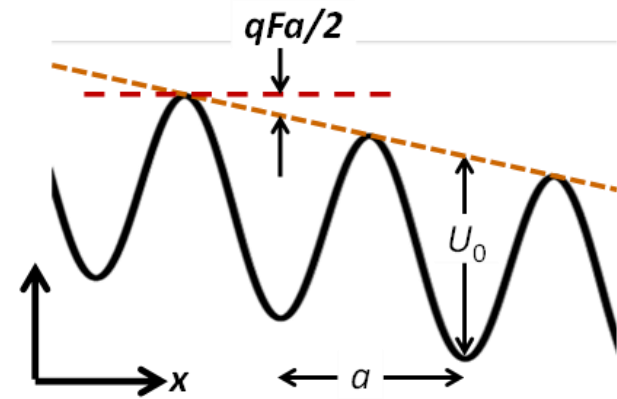


Ion-hopping barrier energy U_0

The Al^{+3} flux through the oxide is limited by the barrier energy U_0 .

The present model found $U_0 = 1.07 \text{ eV}$, which falls within the broad range of previous studies.

study	method	temperature [K]	U_0 [eV]
1966 Harkness [13]	anodization, 180 V	273 – 298	1.30 ± 0.15
1966 Dignam [14]	O_2 exposure	523 – 723	1.6 ± 0.1
1981 Hayden [15]	O_2 exposure	600 – 800	1.17 ± 0.05
1982 Grimblot [16]	O_2 exposure	300 – 600	0.9 ± 0.1

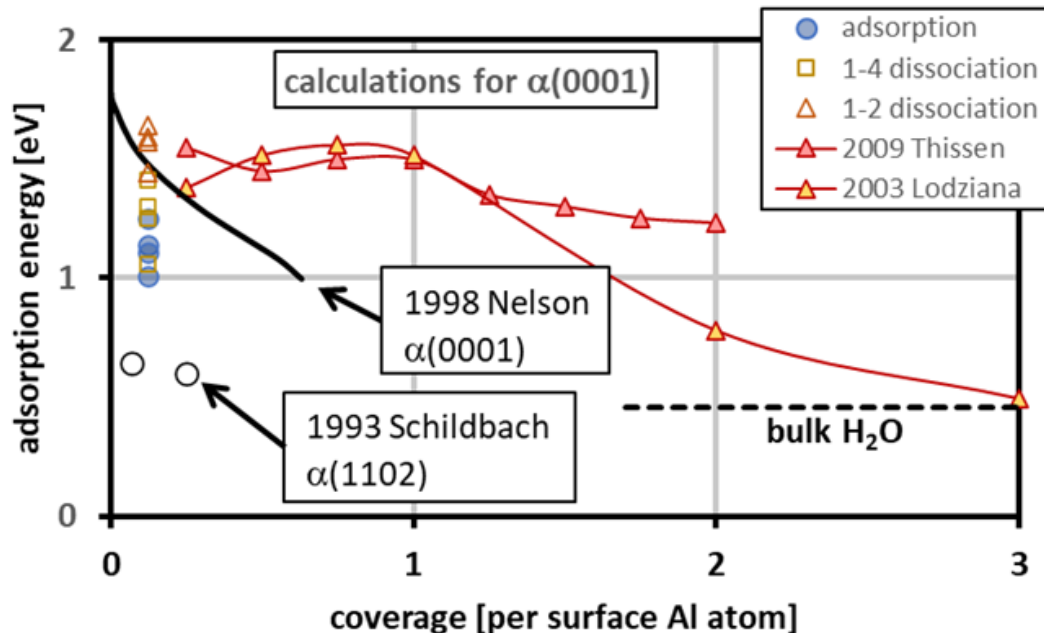


Adsorption energy U_1

An H_2O molecule likely dissociates after desorbing.

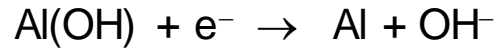
surface	$-U_1$ [eV]	source
$\alpha(0001)$	1.0 to 1.8	measured, calculated
$\alpha(1102)$	0.6	measured
amorphous	broad	?

- The model gives adequate descriptions by fixing $U_1 = -0.98$ eV.
- Increasing $-U_1 > 0.97$ eV does not affect the SURF results.
- Increasing $-U_1$ decreases the water partial pressure P_{H_2O} that describes the sun results.



Ionization energy U_2

The proposed ionization mechanism is the detachment of an OH group from an Al atom and the subsequent ionization of the OH.



The energy change can be estimated as follows.

$$U_2 = E(\text{chemisorbed OH}) - E(\text{adsorbed OH}) - E(\text{electron affinity of OH})$$

$$U_2 \approx E(\text{adsorbed H}_2\text{O}) - E(\text{dissociated H}_2\text{O}) - E(\text{electron affinity of OH})$$

$$U_2 \approx 0.4 \text{ eV} - 1.8 \text{ eV} = -1.4 \text{ eV}$$

- The negative value means that the reaction is favored energetically.
- If the OH is bound strongly to the Al, the ionization energy will be closer to 0 eV.
- The model fit yielded $U_2 = -0.69 \text{ eV}$.

Photodesorption: H_2O /photon yield Y is reasonable

This effect was most important for the SURF exposure at the **lowest pressure** of 2.5×10^{-8} Torr.

Bulk water

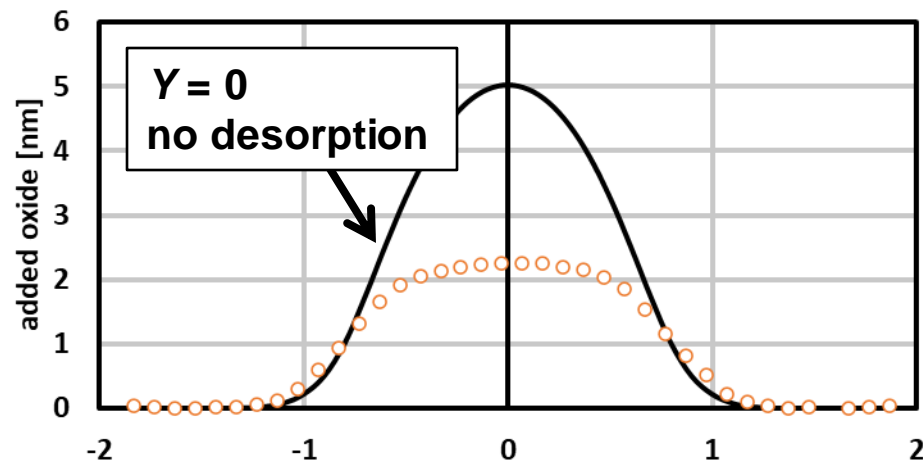
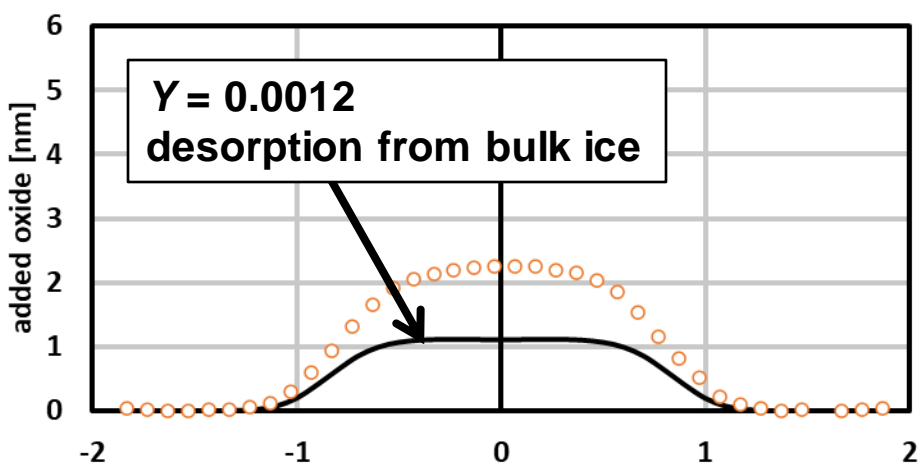
$Y = 0.0012 \pm 0.0006$ (Öberg et al. 2009)

< 1 monolayer of H_2O on Al_2O_3

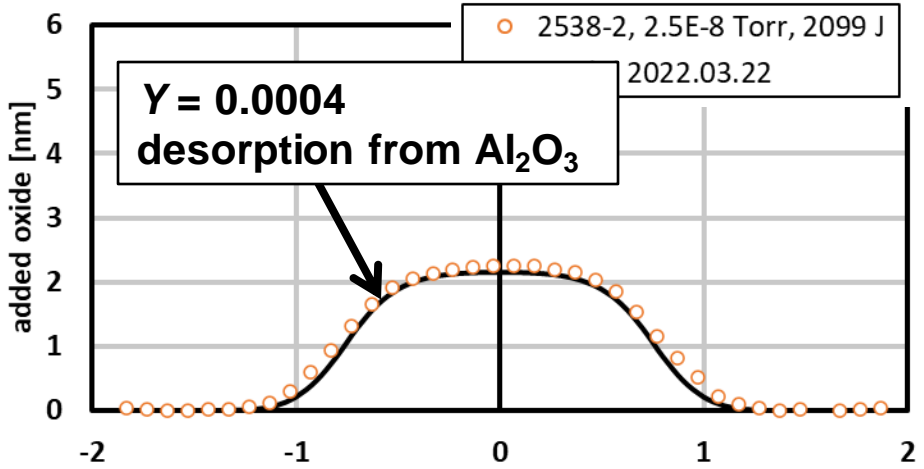
$Y < 0.0012 \pm 0.0006$ (H_2O binds strongly to Al_2O_3)

Fitted value in the model

$Y = 0.0003$



○ 2538-2, 2.5E-8 Torr, 2099 J
— model 2022.03.22



○ 2538-2, 2.5E-8 Torr, 2099 J
— model 2022.03.22
Al oxide growth

○ 2538-2, 2.5E-8 Torr, 2099 J
— model 2022.03.22

position [mm]
Al oxide growth



Al³⁺ ion current

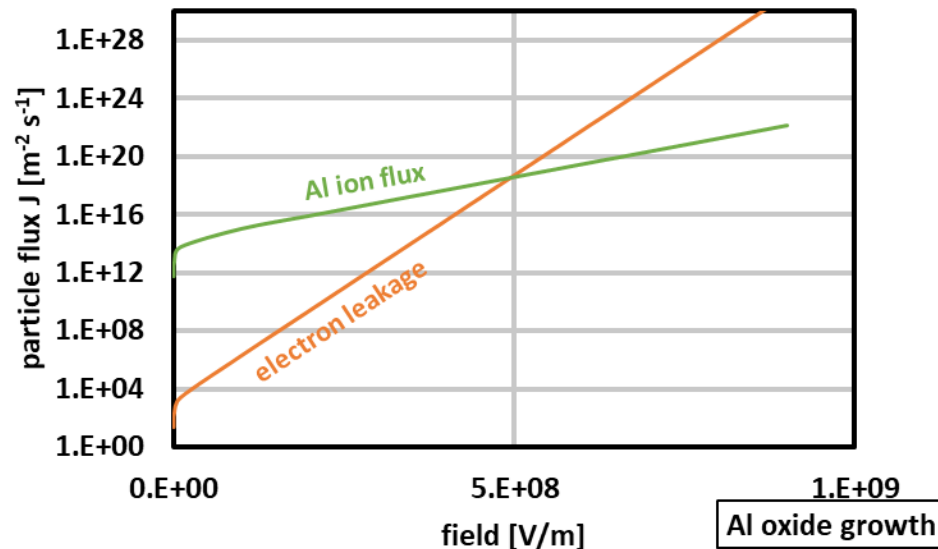
The model assumes that the surface charge, held by OH⁻ ions, is decreased by:

- thermally driven conversion of charged OH⁻ to neutral OH
- electron leakage through the oxide (Fowler-Nordheim tunneling or Poole-Frenkel emission)
- arrival of positively charged Al³⁺ ions

The electron leakage J_{leak} and the Al³⁺ ion flux J_{Al} can both be described by

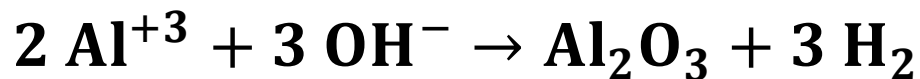
$$J_x(F) = J_x \sinh\left(\frac{F}{F_x}\right)$$

The Al³⁺ ion flux is more important for fields up to 500 MV/m, and the model says that the SURF exposures never created a field larger than 400 MV/m.



Combination of ions

The reaction of cations and anions is assumed to be fast and irreversible.



What about the hydrogen?

Hydrogen release has been seen during measurements of adsorption of water of Al oxide. The amount depends on the degree of H₂O dissociation.

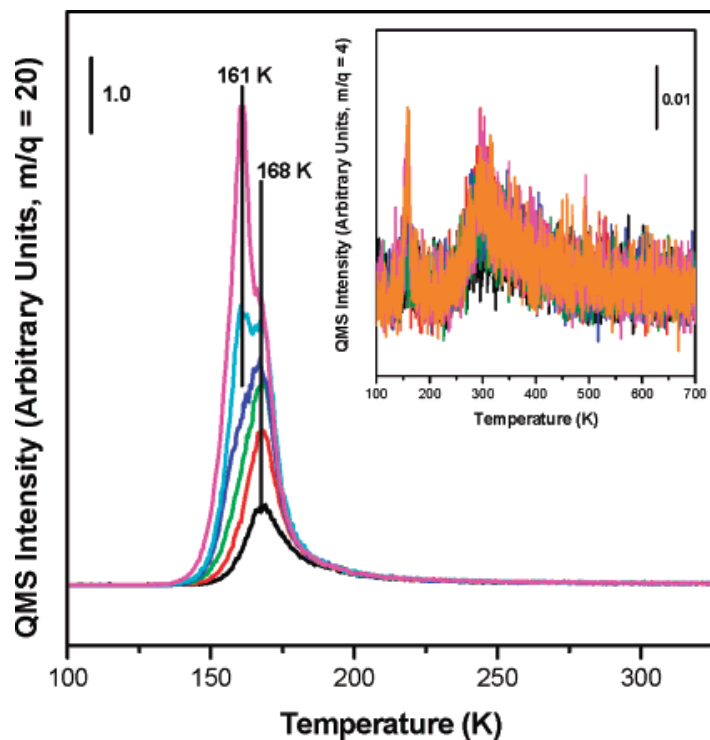


Figure 2. TPD data for various exposure (0.35-2.3 ML) of D₂O (AMU = 20) adsorbed on an ordered, ultrathin Al₂O₃/NiAl(110) film surface. D₂O was deposited at 100 K and the heating rate was 1 K/s. The inset shows D₂ desorption after adsorption of D₂O.

2007 [Yi, Szanyi] "D₂O adsorption on an ultrathin alumina film on NiAl(110)"

Excitation and emission of electron into the oxide

1905: Classical electron theory of metals

All of the emitted electrons have nearly the same energy.

$$E = h\nu - \phi$$

← metal-oxide work function

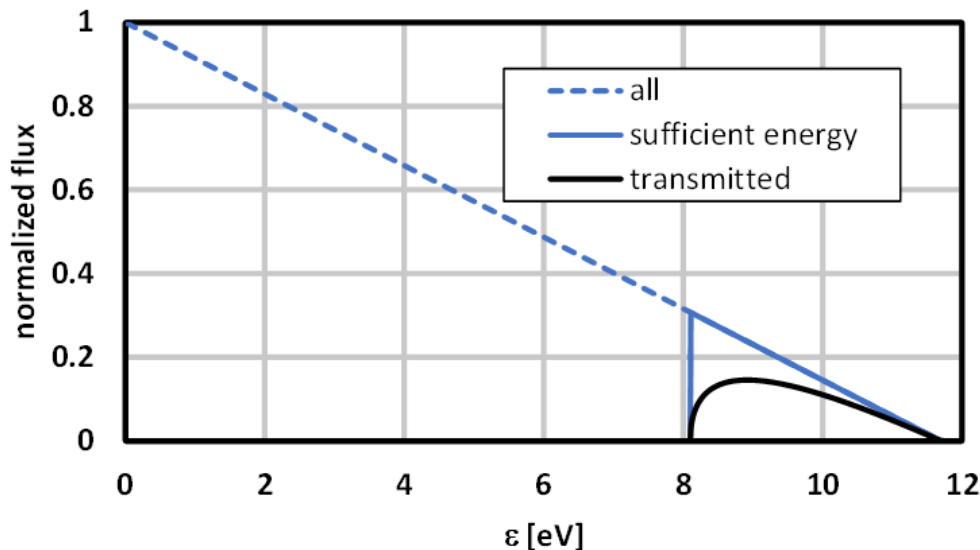
~1930: Free electron gas

Fermi-Dirac statistics were applied to the free-electron gas by Nordheim (1928), Fowler & Nordheim (1931), DuBridge (1933). The emitted electrons have a broad distribution.

Later: Improvements

Account for scattering of the electrons in the bulk, excitation of plasmons, and the effect of surface states.

Excitation and emission of electron into the oxide



Example

Fermi energy

$$\varepsilon_F = 11.7 \text{ eV}$$

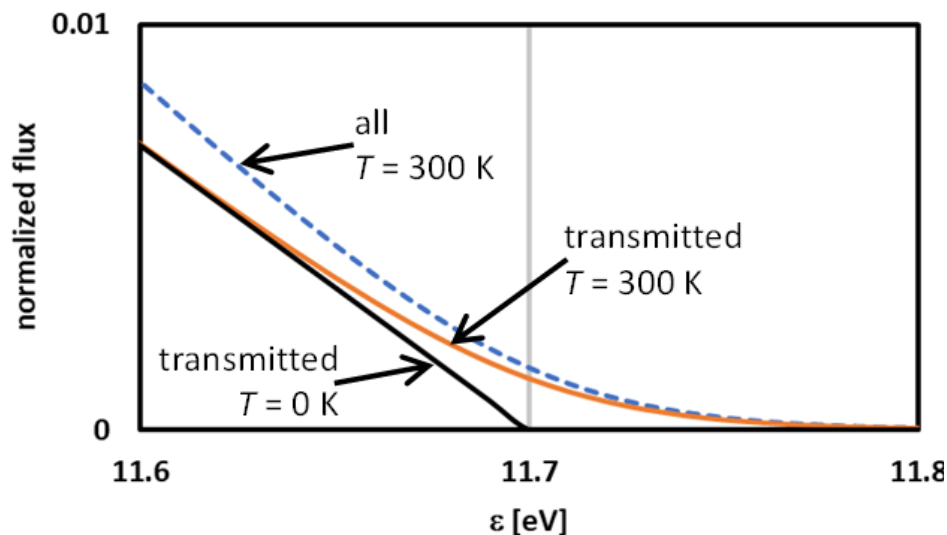
work function

$$\phi = 2.6 \text{ eV}$$

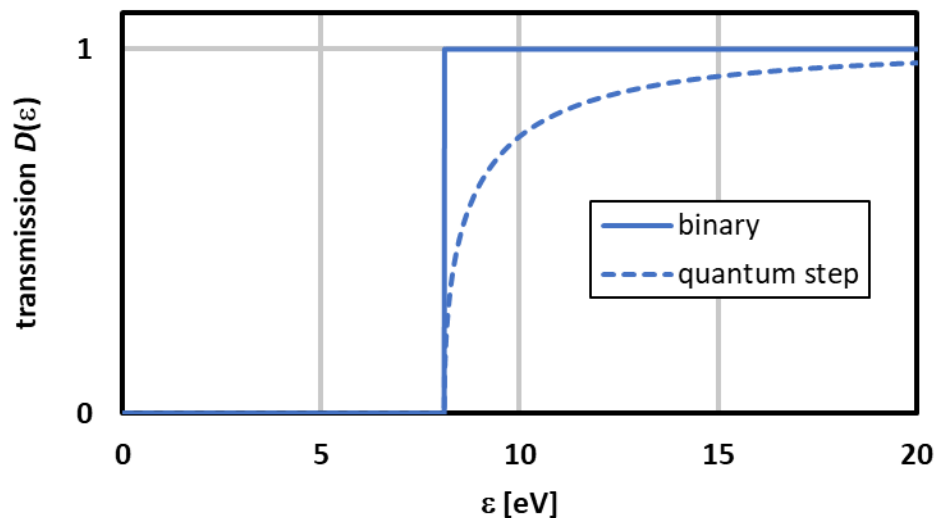
photon energy

$$h\nu = 6.3 \text{ eV } (\lambda = 200 \text{ nm})$$

Only some of the excited electrons emit into the oxide.



The correction for $T = 300 \text{ K}$ is tiny.

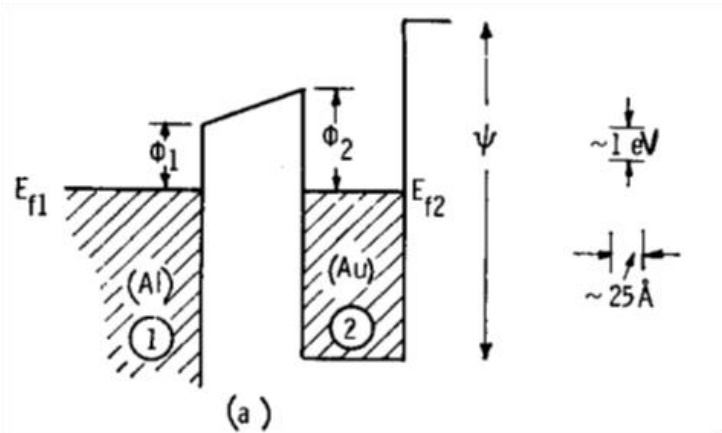


Some electrons are reflected. **NIST**

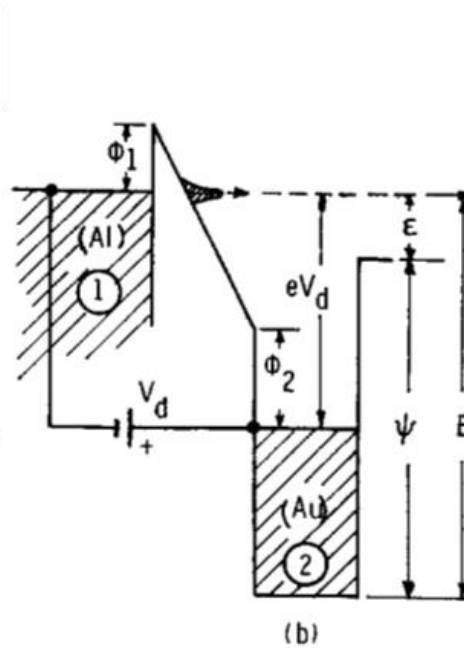
Electron scattering in the oxide: evidence

Evidence in the literature for electron scattering in Al_2O_3

- photoelectrons through thin layers of Al_2O_3
- photoemission from metal-oxide-metal (MIM) sandwiches
- I-V curves of MIM sandwiches



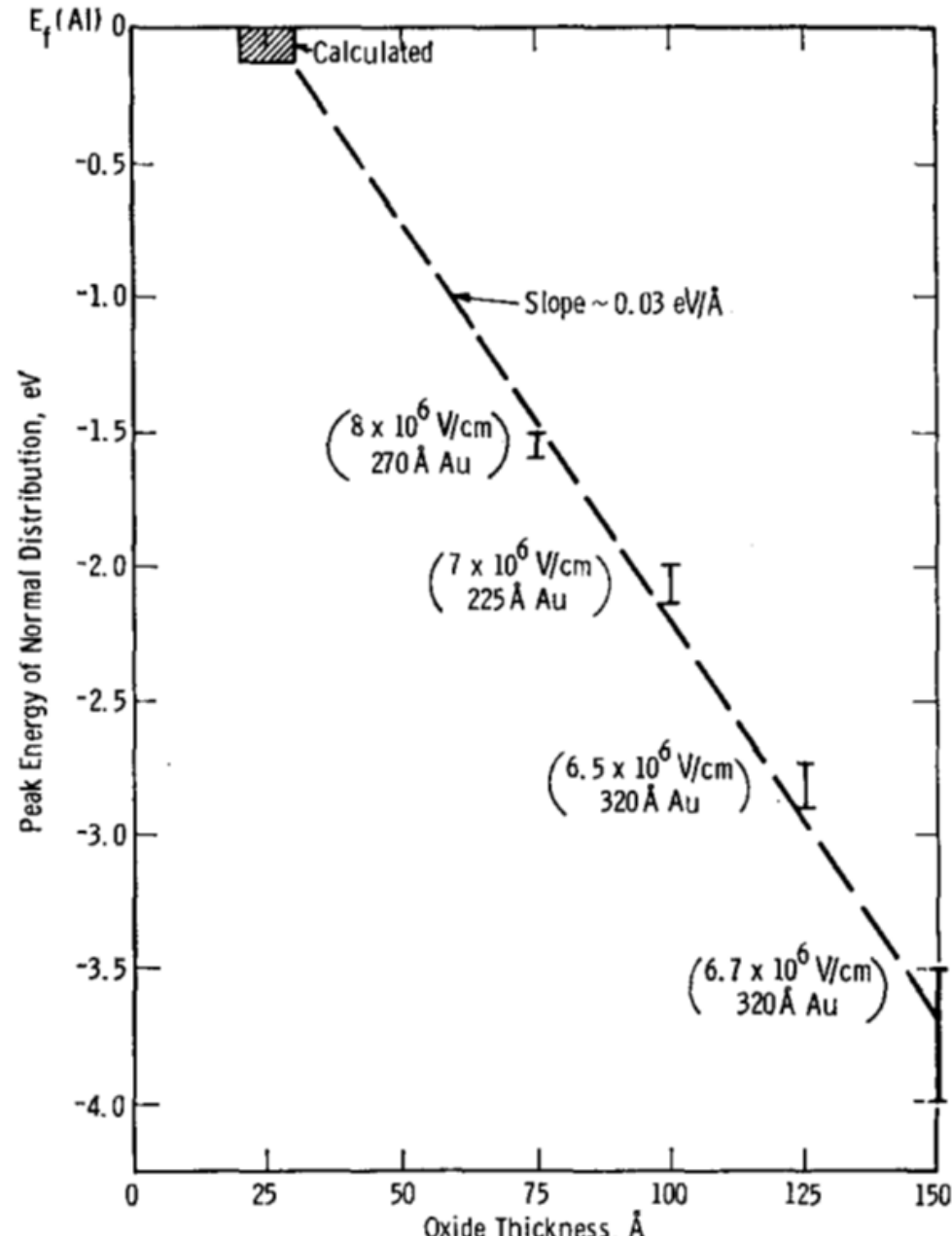
no applied voltage



applied voltage V_d

“Potential in an Al- Al_2O_3 -Au sandwich” (Handy 1966)

Electron scattering in the oxide: evidence



Handy (1968)

“Hot electron energy loss in tunnel cathode structures”

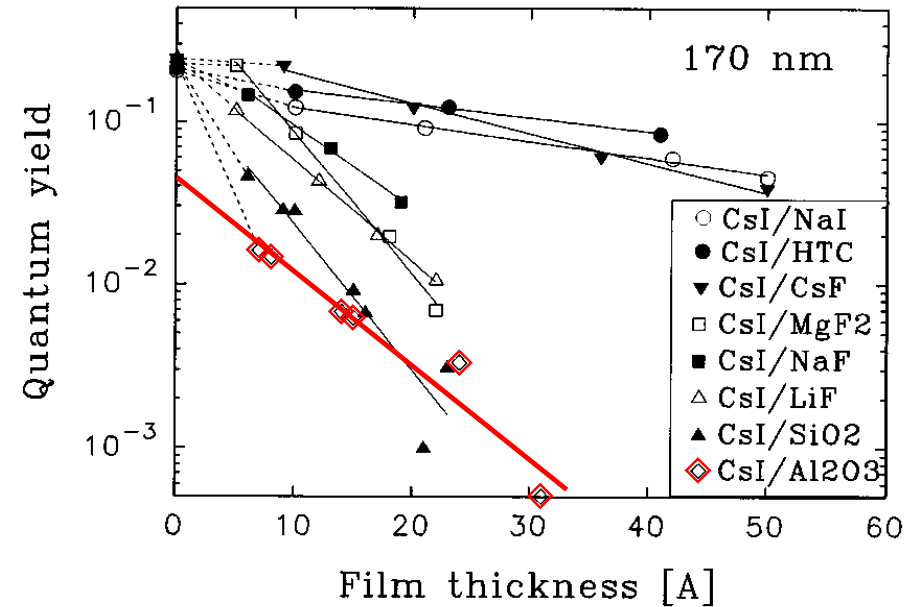
Peak energy of emitted electrons decreased linearly with oxide thickness.

collision loss

1D mean free path

$$E_{\text{phonon}} \equiv 0.1 \text{ eV}$$
$$L = 0.4 \text{ nm}$$

Electron scattering in the oxide: evidence



Buzulutskov, Breskin, & Chechik (1998)

“Photoemission through thin dielectric coating films”

Photoemission for various films on CsI substrate.

photons $h\nu = 7.3 \text{ eV}$
attenuation length $L_{\text{att}} = 0.9 \text{ nm}$
1D mean free path $L = ?$

Electron scattering in the oxide: simulation

The simulation output was the fraction f_X of electrons that reached the oxide-vacuum surface for a given combination of mean free path L , collision loss E_{phonon} , electric field F . The outputs could be represented by the simple empirical function f_X .

The function $f(X/X_{\text{mid}})$ accounts for the finite energy of the electrons.

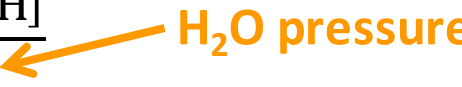

The parameter X_{mid} depends on L , E_{phonon} , F in a regular way.

$$f_X = \frac{n_e(X)}{n_e(L)} \equiv \frac{f(X/X_{\text{mid}})}{X/L} = \frac{1}{(X/L)[1+(X/X_{\text{mid}})^4]}$$

The factor X/L is expected for diffusion.

Surface reactions: $p_{H_2O} + [e] \rightarrow$ surface charge

$[Z] \equiv$ surface concentration of species Z

equilibrium constant	$K_1 = \frac{[OH S H]}{[S]p}$	
equilibrium constant	$K_2 = \frac{[OH^- S H]}{[OH S H][e]}$	
concentration of all sites	$M = [S] + [OH S H] + [OH^- S H]$	
concentration of open sites	$[S] = M(1 + K_1p + K_1pK_2[e])^{-1}$	
concentration of charged sites	$\sigma = [OH^- S H] = K_2[e][H_2O S] = K_2[e]K_1p[S]$	

Combine the above to obtain the fraction of sites that are charged:

$$\frac{\text{charged sites}}{\text{all sites}} = \frac{\sigma}{M} = \frac{K_1pK_2[e]}{1 + K_1p + K_1pK_2[e]}$$

Transport of Al^{+3} : Two approximations

Ion flux:

$$J = 4av \exp\left(-\frac{U}{kT}\right) \sinh\left(\frac{qaF}{kT}\right) \left[n - \frac{kT}{qF} \frac{dn}{dx}\right]$$

1. Small electric field F :

$$J = 4av \exp\left(-\frac{U}{kT}\right) \left(\frac{qaF}{kT}\right) \left[n - \frac{kT}{qF} \frac{dn}{dx}\right]$$

$$J = \mu F n - D \frac{dn}{dx}$$

electric mobility

diffusivity

2. Negligible diffusion:

$$J = \mu F n$$

where

$$\mu = \frac{4qa^2v}{kT} \exp\left(-\frac{U}{kT}\right)$$

Electron flux attenuation depends on electric field

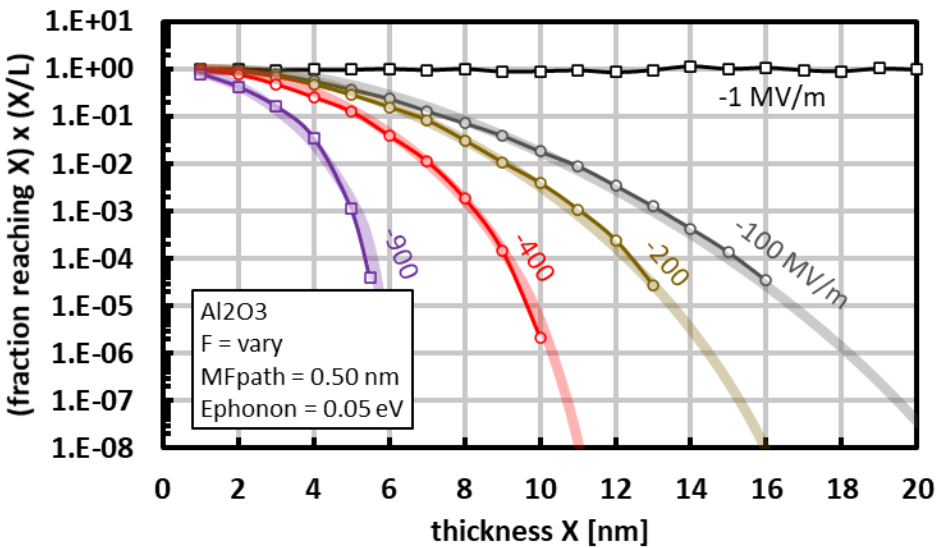
If the electric field is weak:

Each electron injected into the oxide does a random walk until it reaches either the metal or the vacuum surface. The resulting attenuation is described by diffusion, and the fraction that reaches the oxide-vacuum surface at position X is simply L/X , where L is the electron mean free path.

If the electric field is strong:

Each electron does a random walk until it loses all its energy to collisions to optical phonons. If it has not yet reached the vacuum surface, the resulting thermalized electron is swept back to the metal. The fraction that reaches the oxide-vacuum surface depends on the field and oxide thickness. A “strong” field F is one for which

$$F > \frac{kT}{eL} = \frac{(0.026 \text{ eV})}{(\sim 1 \text{ nm})} = 26 \text{ MV/m}$$

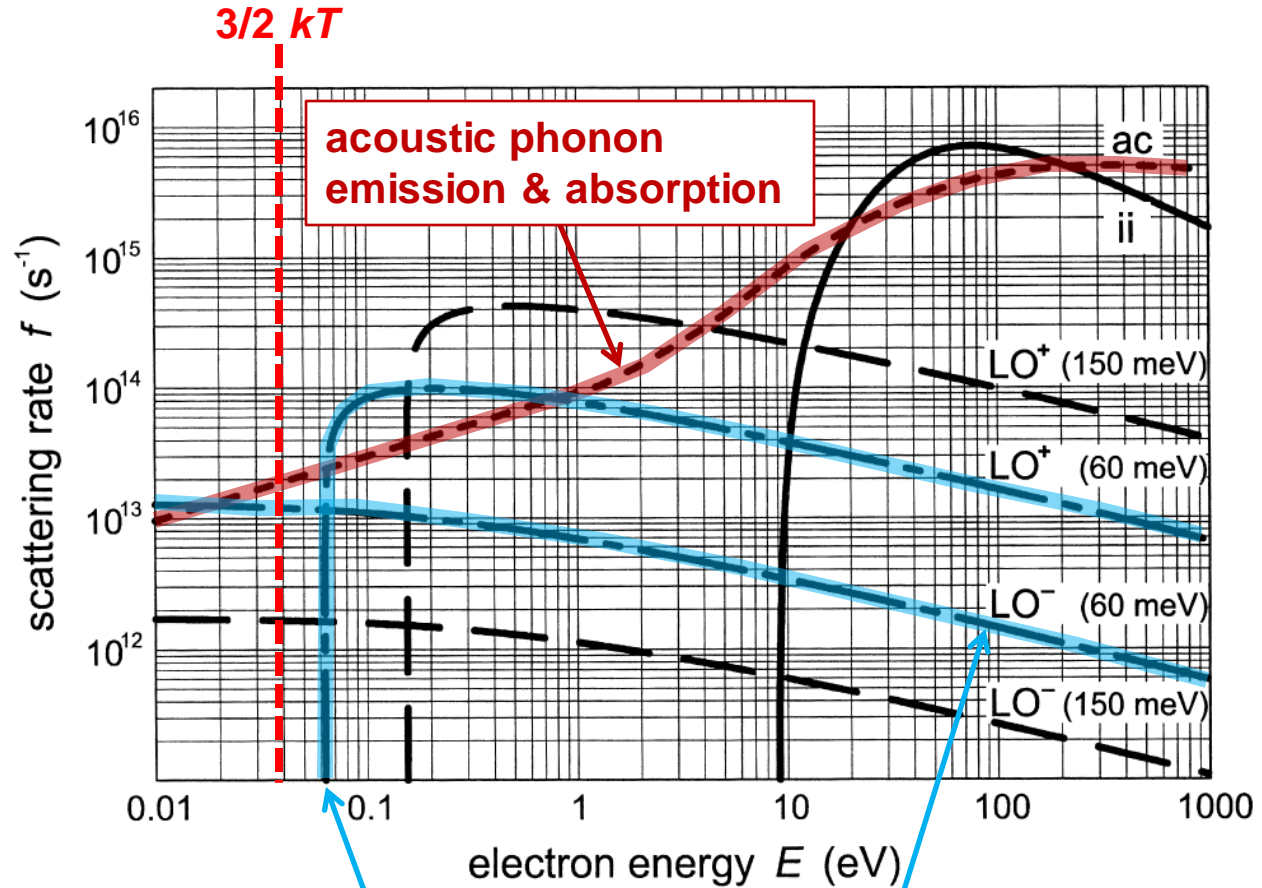


Monte Carlo calculations of the electron flux attenuation for electric fields ranging from -100 MV m^{-1} to -900 MV m^{-1} . The description of the calculations is overlaid on four curves. The points for -1 MV m^{-1} represent scattering in a weak field.

These results are multiplied by X/L so that the result for simple diffusion is 1.

A thermalized electron sees just acoustic phonons

Fitting, Schreiber, Kuhr. von Czarnowski, Journal of Electron Spectroscopy and Related Phenomena 119, 35–47 (2001).
“Attenuation and escape depths of low-energy electron emission”



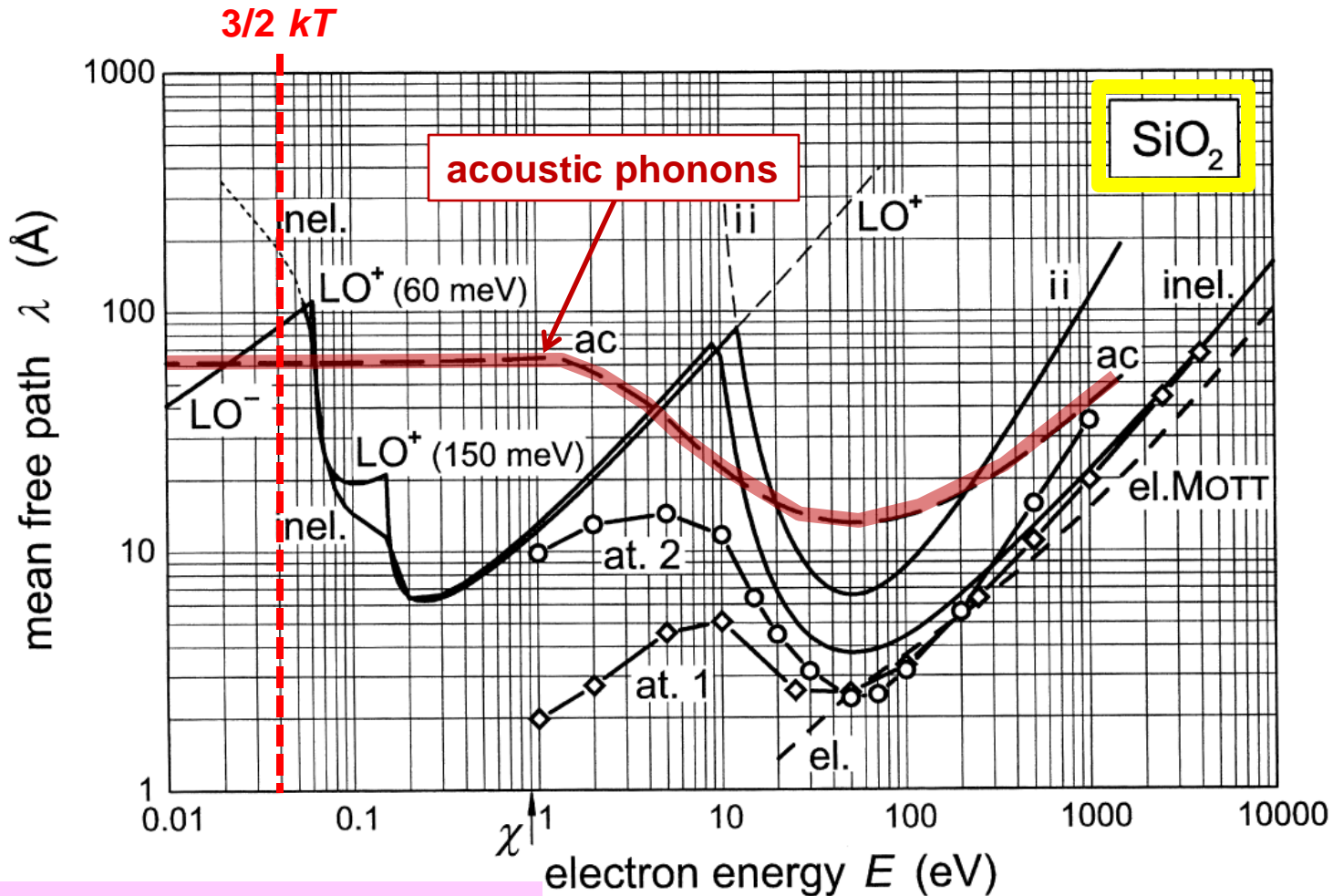
Minimum energy to emit an optical phonon energy

SiO₂ 0.06 eV

Al₂O₃ 0.05 eV

A thermalized electron has a long mean free path

Fitting, Schreiber, Kuhr. von Czarnowski, Journal of Electron Spectroscopy and Related Phenomena **119**, 35–47 (2001).
 “Attenuation and escape depths of low-energy electron emission”



mean free path at low energy

SiO ₂	6 nm
Al ₂ O ₃	10 nm (fit to SURF results)

Al³⁺ ion current

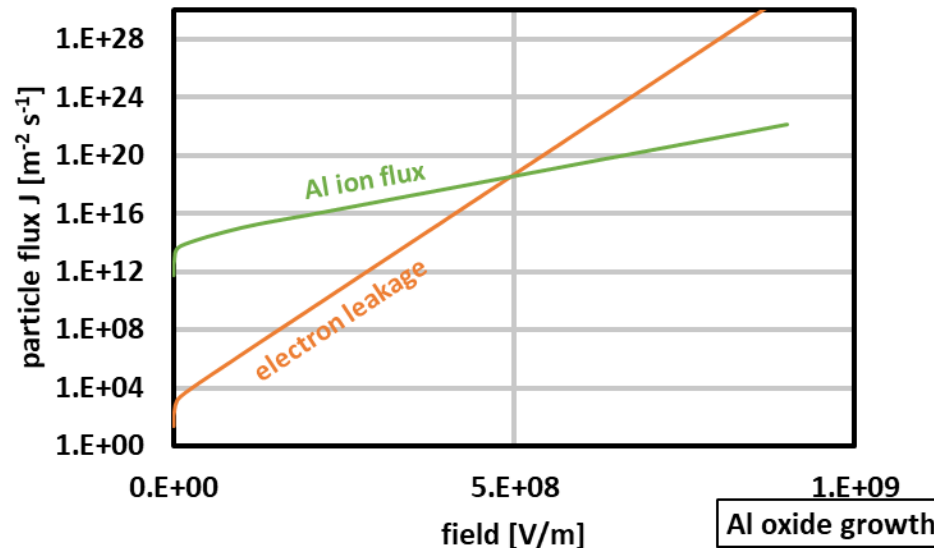
The model assumes that the surface charge, held by OH⁻ ions, is decreased by:

- thermally driven conversion of charged OH⁻ to neutral OH
- electron leakage through the oxide (Fowler-Nordheim tunneling or Poole-Frenkel emission)
- arrival of positively charged Al³⁺ ions

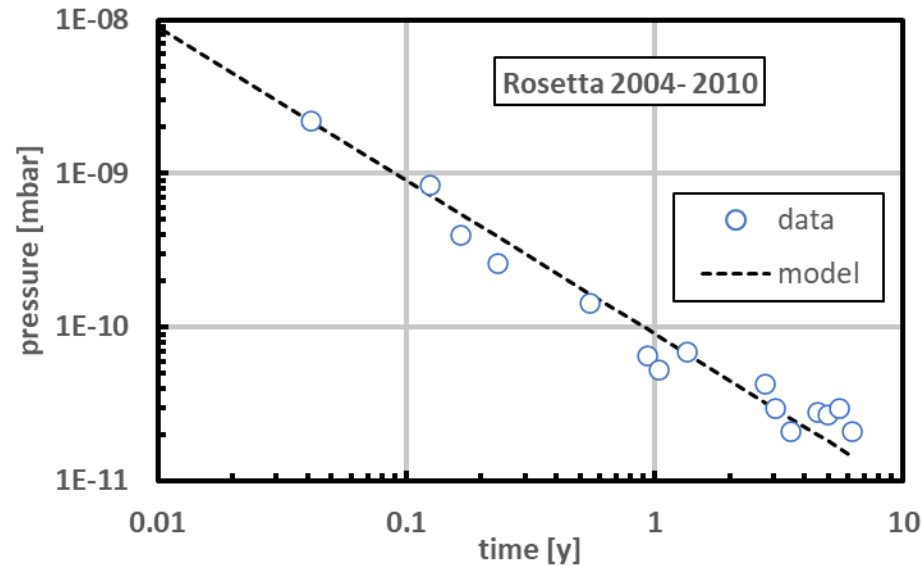
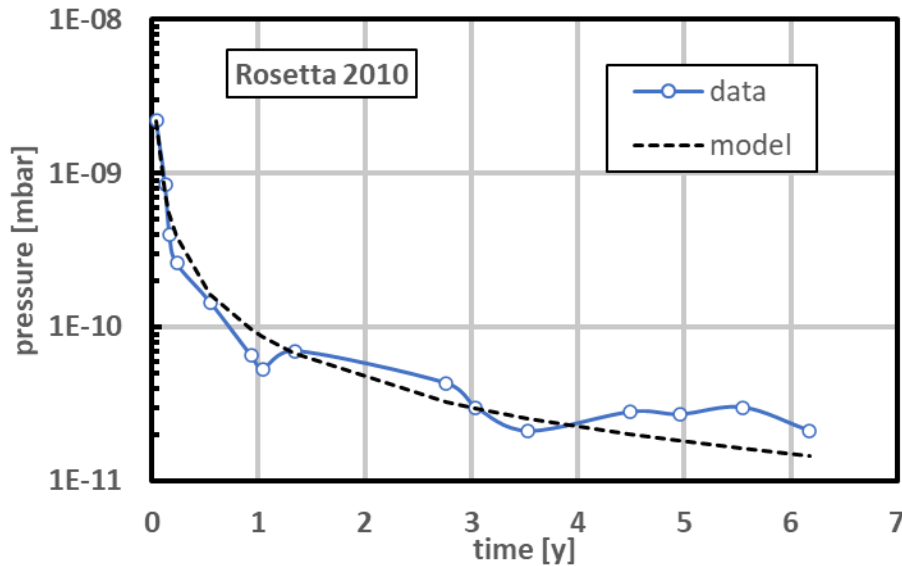
The electron leakage J_{leak} and the Al³⁺ ion flux J_{Al} can both be described by

$$J_x(F) = J_x \sinh\left(\frac{F}{F_x}\right)$$

The Al³⁺ ion flux is more important for fields up to 500 MV/m, and the model says that the SURF exposures never created a field larger than 400 MV/m.



Enough water outgassing to cause oxidation



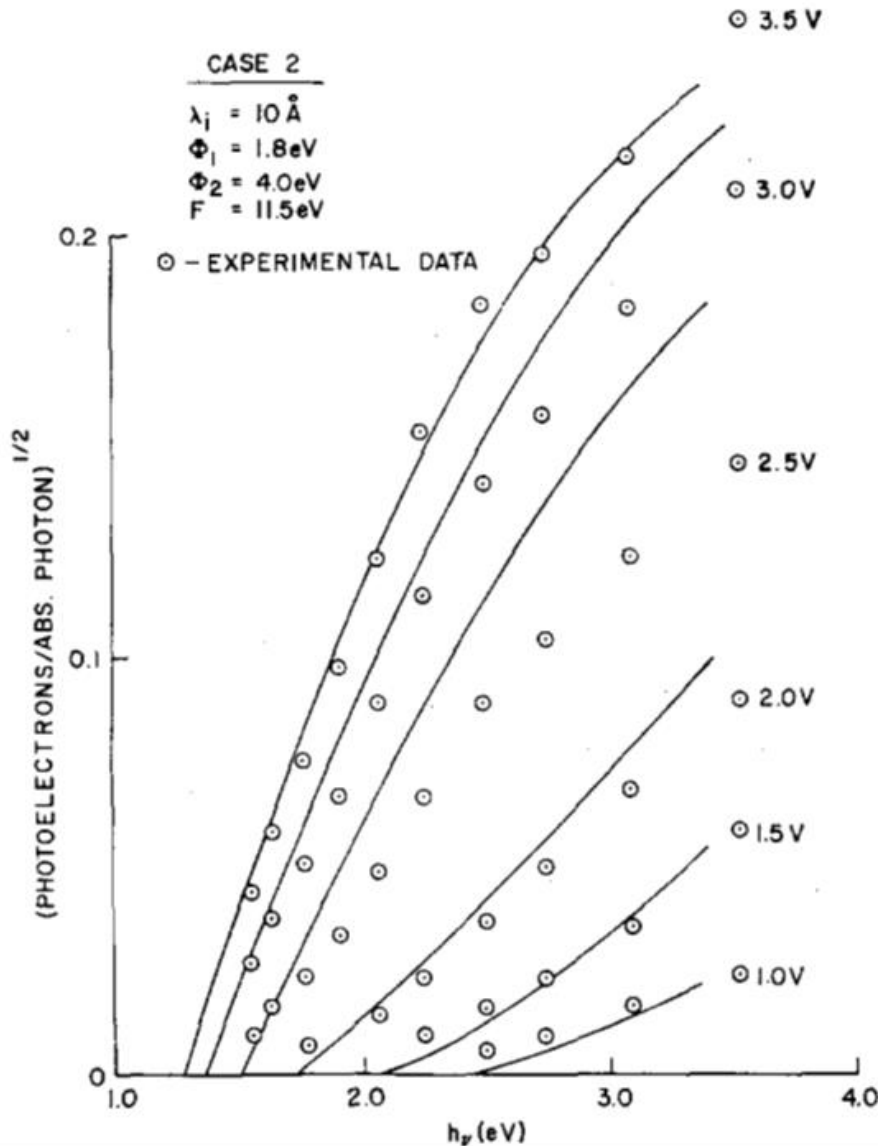
The comet probe Rosetta is an example of long-lived outgassing:

- The pressure measured was likely water.
- The pressure decayed slowly, as $1/t$.
- The pressure after 6 years was 2×10^{-11} mbar.

The initial degradation seen on the SDO satellite:

- Corresponds to an oxide growth rate of 13 nm/year.
- This requires an H₂O pressure of at least 6×10^{-12} mbar.

Electron scattering in the oxide: Literature



Schuermeyer, Young, and Blasingame (1968)

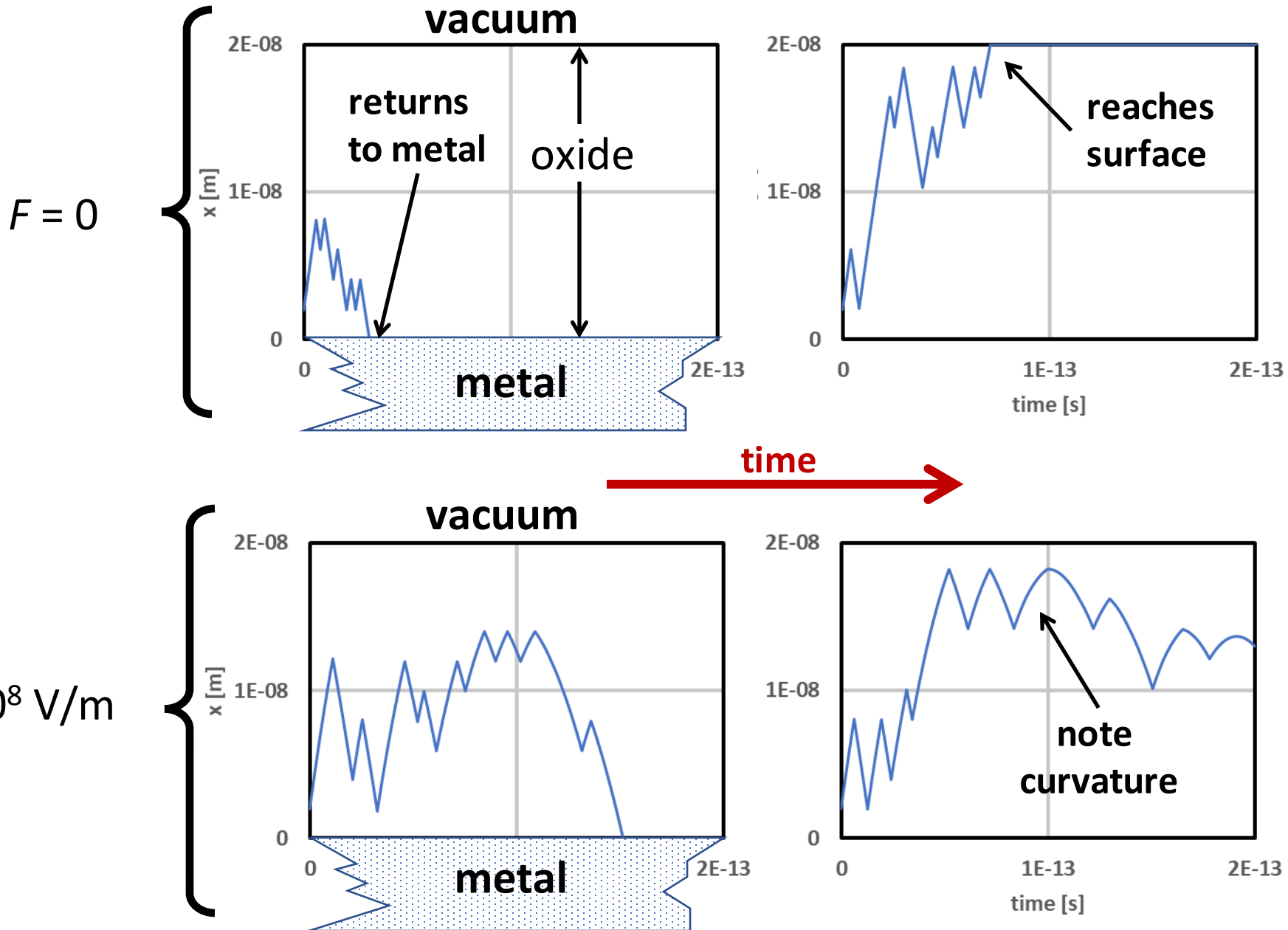
“Photovoltage measurements on an Al-Al₂O₃-Al thin-film sandwich”

Scattering model fit to measured photocurrent as a function of photon energy and bias voltage.

photons $1.5 \text{ eV} < h\nu < 3.5 \text{ eV}$
collision loss $E_{\text{phonon}} \equiv 0.1 \text{ eV}$

mean free path $L = 1.0 \pm 0.2 \text{ nm}$

Electron scattering in the oxide: Monte Carlo



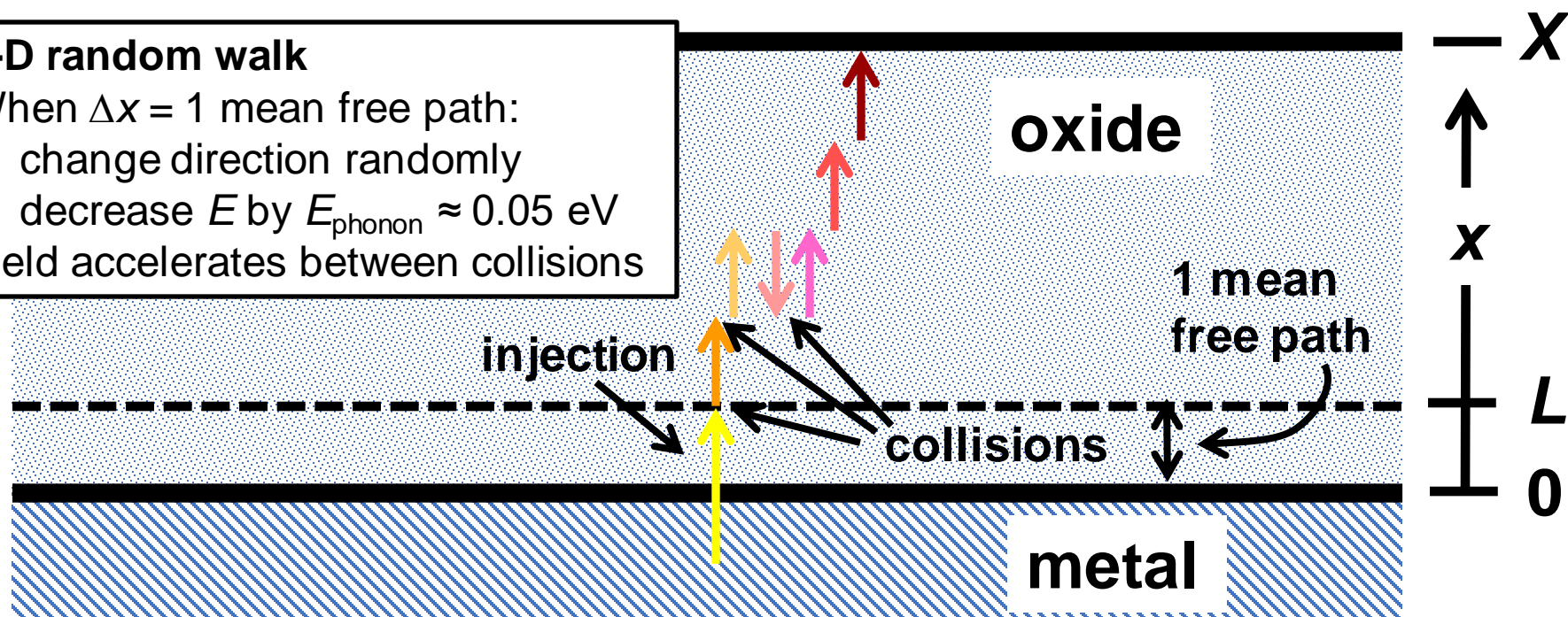
Electron scattering in the oxide: 1D Monte Carlo

1-D random walk

When $\Delta x = 1$ mean free path:

- change direction randomly
- decrease E by $E_{\text{phonon}} \approx 0.05$ eV

Field accelerates between collisions



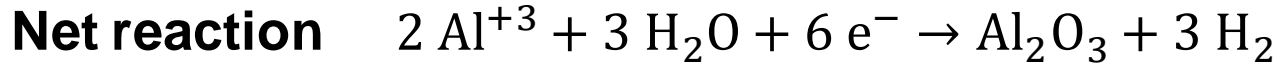
simulation inputs

X	oxide thickness
L	1D mean free path
E_{phonon}	energy loss per collision
F	electric field in the oxide
$\phi_{\text{oxide-vac}}$	oxide-vacuum work function
$N(E)$	energy distribution of injected electrons
n_{max}	number of random electron trajectories

simulation output

f_x	fraction of electrons that reach $x = X$
-------	--

Combination of Al^{+3} with OH^-



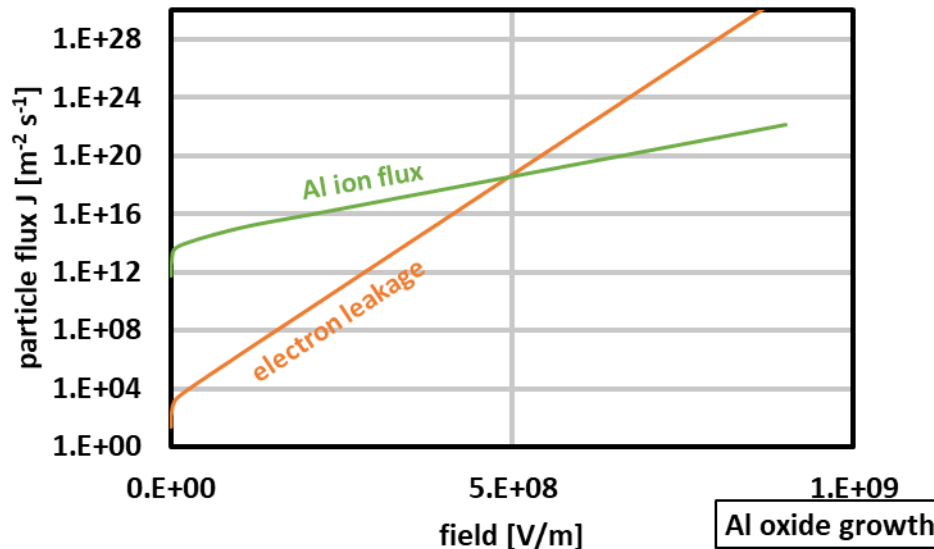
The density of surface charge is decreased by:

- Thermally driven conversion of charged OH^- to neutral OH .
- Electron leakage through the oxide (Fowler-Nordheim tunneling or Poole-Frenkel emission).
- Arrival of positively charged Al^{+3} ions.

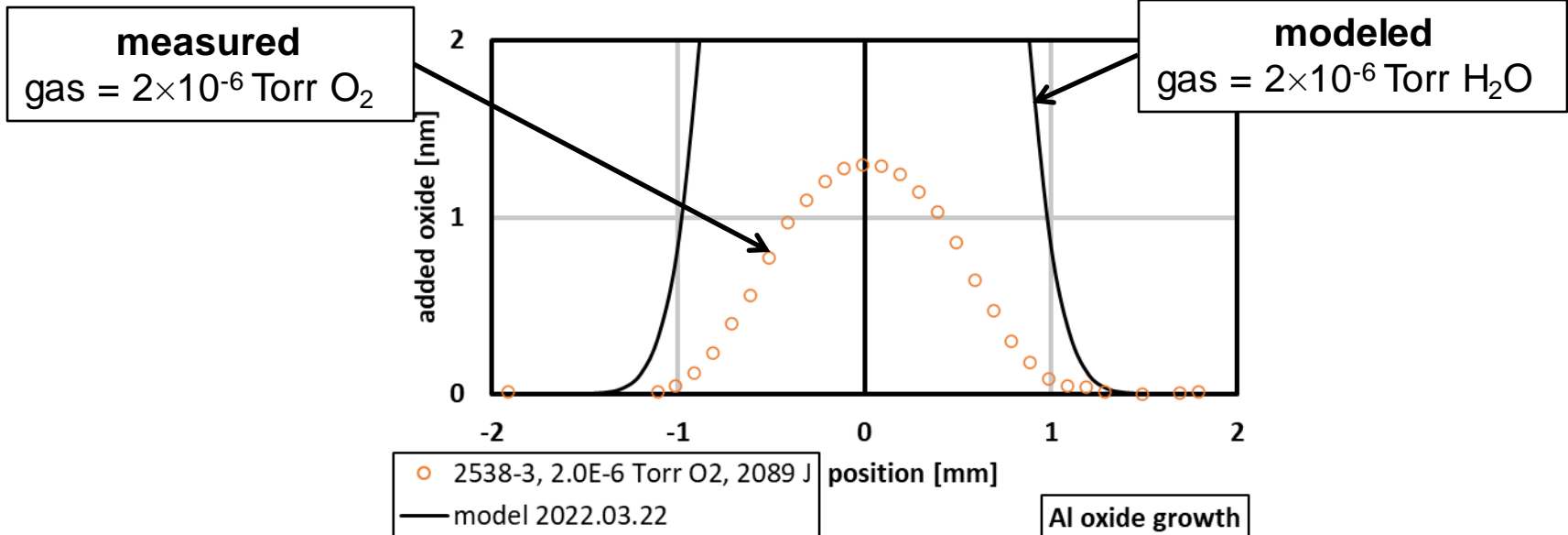
The electron leakage J_{leak} and the Al^{+3} ion flux J_{Al} can both be described by

$$J_x(F) = J_x \sinh\left(\frac{F}{F_x}\right)$$

Electron leakage was negligible for the SURF exposures because $F < 300 \text{ MV/m}$.

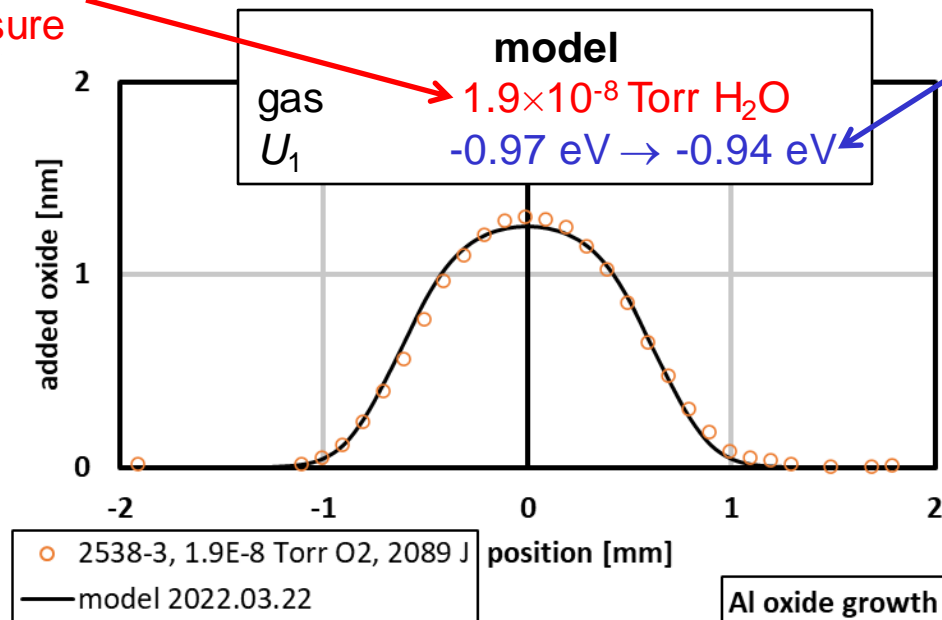


2538-3: H₂O is a better oxidant than O₂



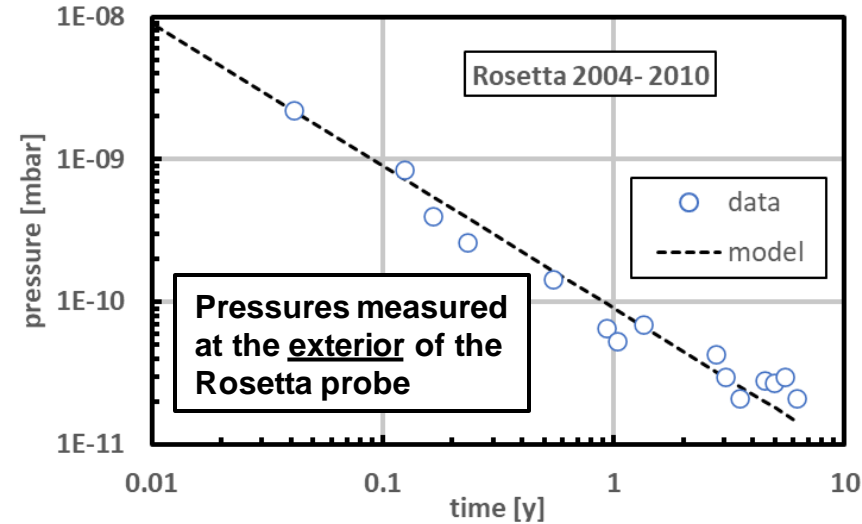
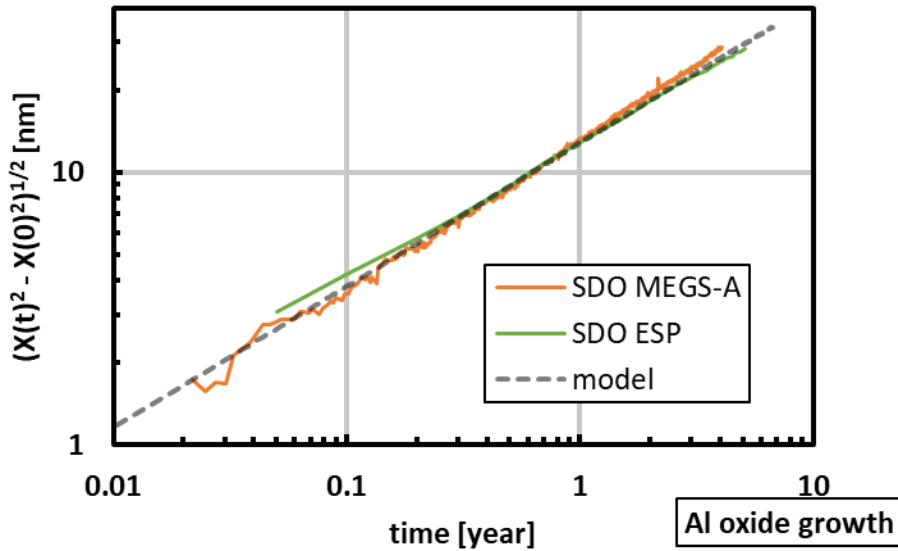
Similar to background H₂O pressure

Reduced absorption energy

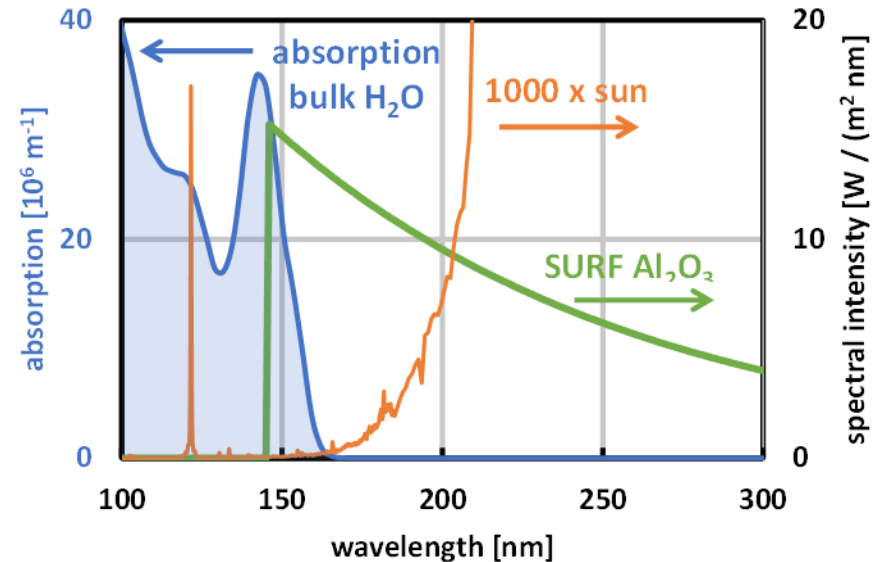
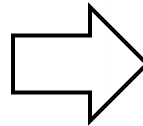


SDO oxide growth

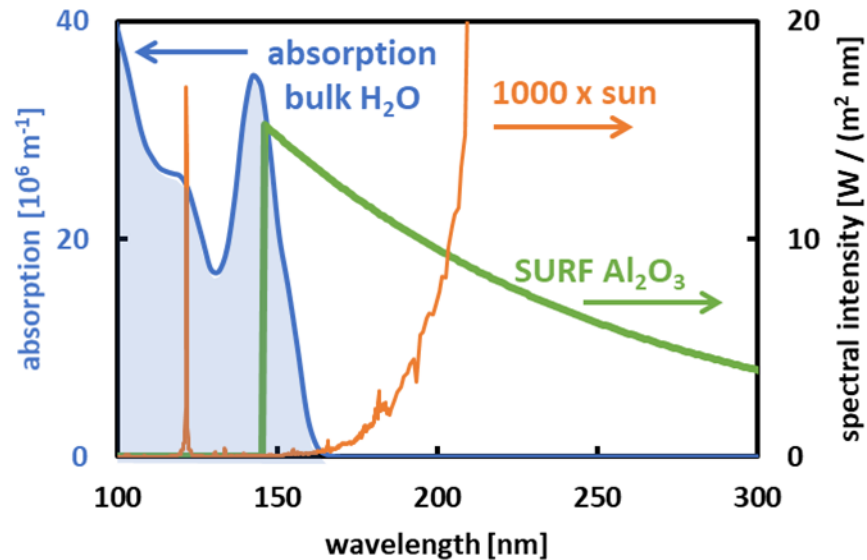
- The model agrees with the SDO data if one sets $P_{\text{H}_2\text{O}} = 2.5 \times 10^{-9}$ mbar.
- This value seems reasonable, but was the outgassing pressure really constant inside SDO?
- Increasing absorption energy U_1 decreases $P_{\text{H}_2\text{O}}$. SURF results are insensitive to $-U_1 > 0.97$ eV.



Photodesorption was not important on SDO because it occurred only at the Lyman-alpha wavelength.



SDO oxide growth



Photodesorption was not important on SDO because it occurred only at the Lyman-alpha wavelength.

Photodesorption: H_2O /photon yield Y is reasonable

This effect was most important for the SURF exposure at the **lowest pressure** of 2.5×10^{-8} Torr.

Bulk water

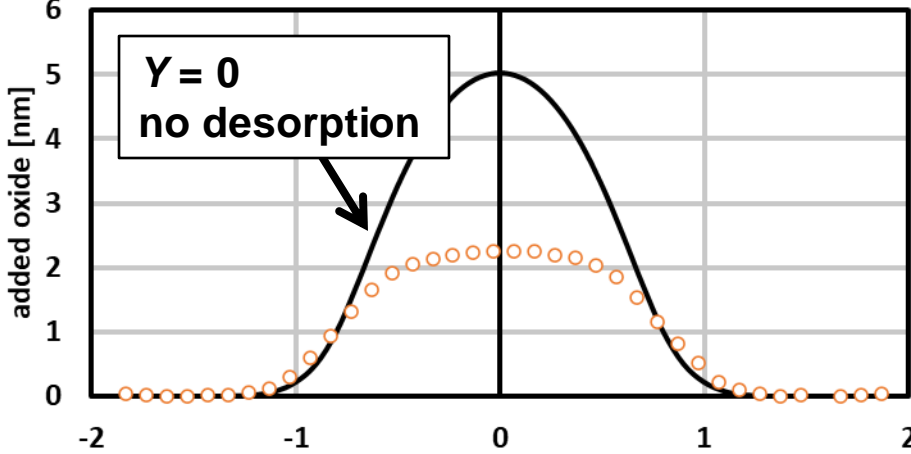
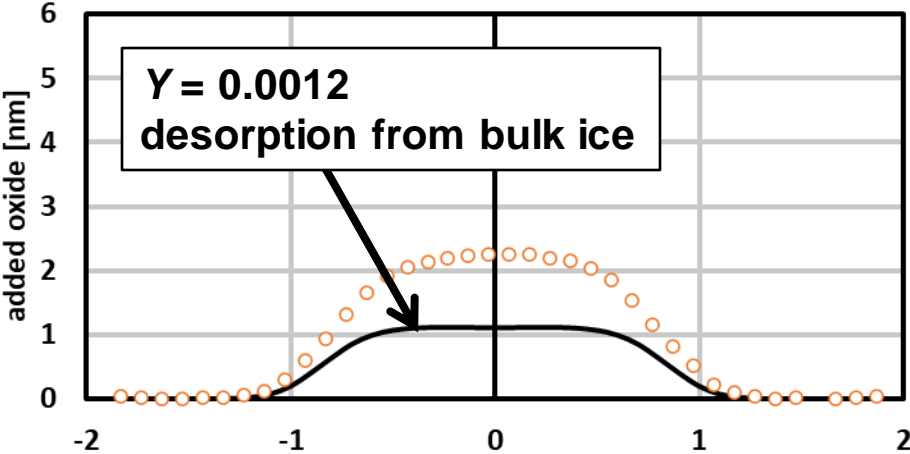
$$Y = 0.0012 \pm 0.0006 \text{ (Öberg et al. 2009)}$$

< 1 monolayer of H_2O on Al_2O_3

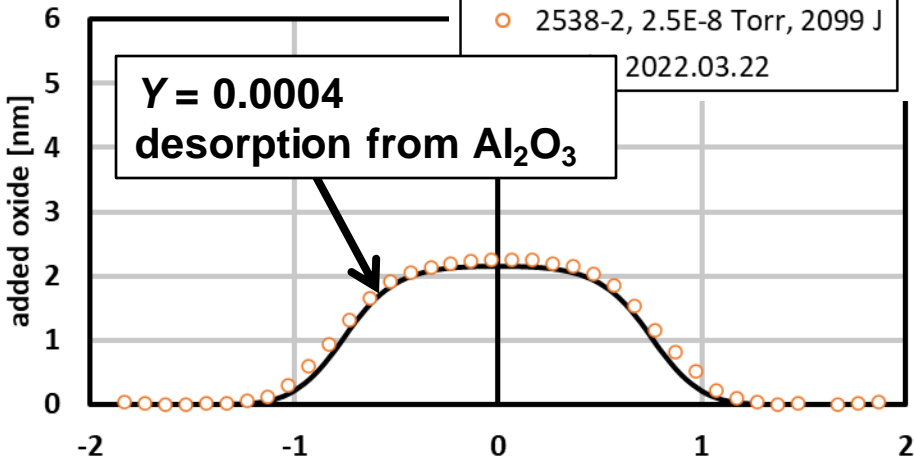
$$Y < 0.0012 \pm 0.0006 \text{ (H}_2\text{O binds strongly to Al}_2\text{O}_3\text{)}$$

Fitted value in the model

$$Y = 0.0003$$



○ 2538-2, 2.5E-8 Torr, 2099 J
— model 2022.03.22



○ 2538-2, 2.5E-8 Torr, 2099 J
— model 2022.03.22

position [mm]

Al oxide growth

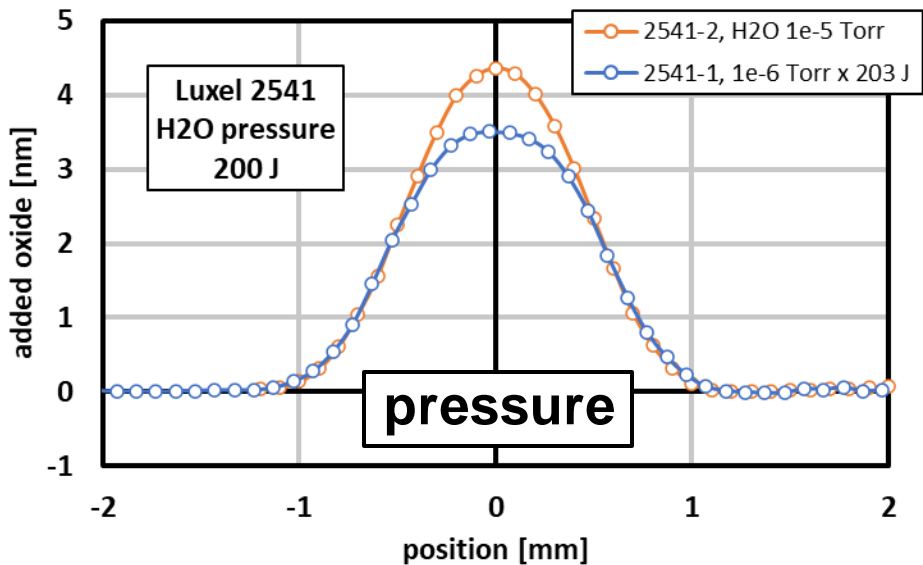
○ 2538-2, 2.5E-8 Torr, 2099 J
— model 2022.03.22

position [mm]

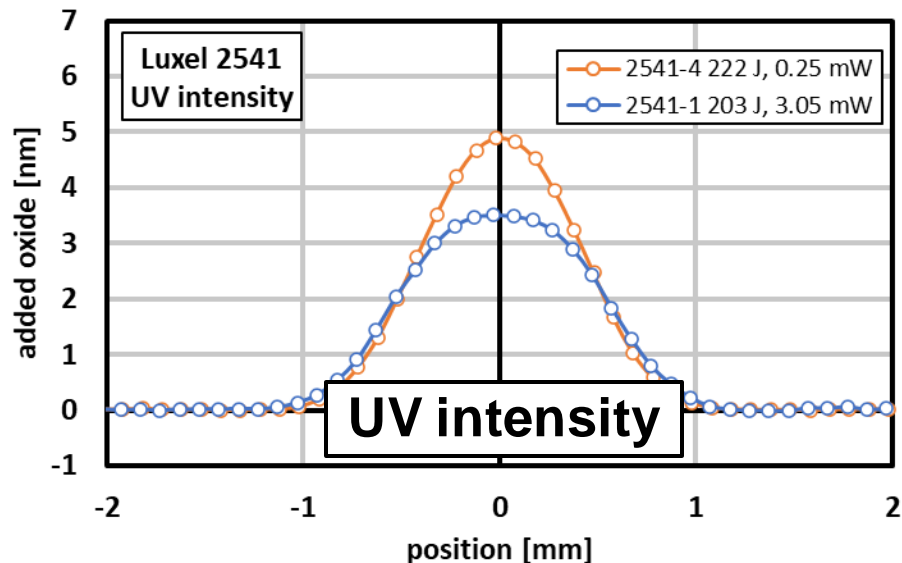
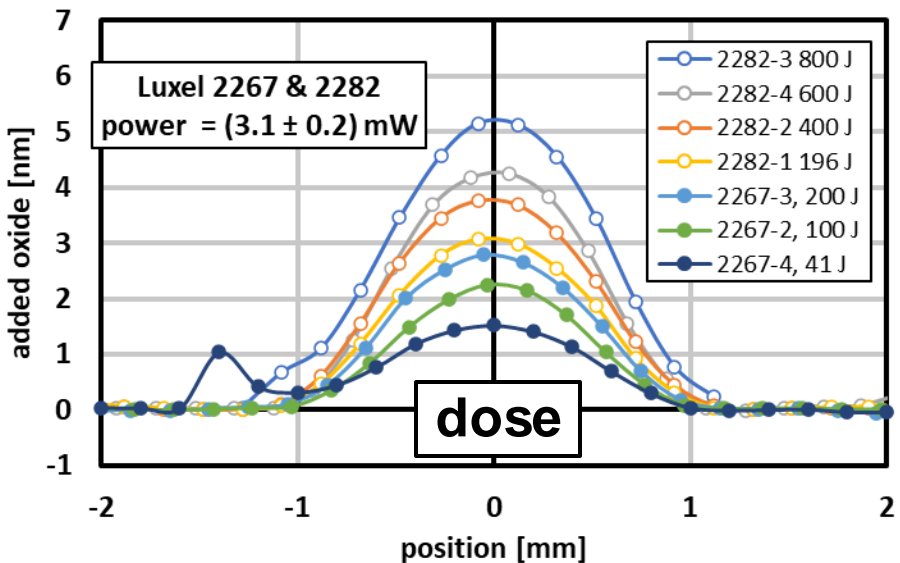
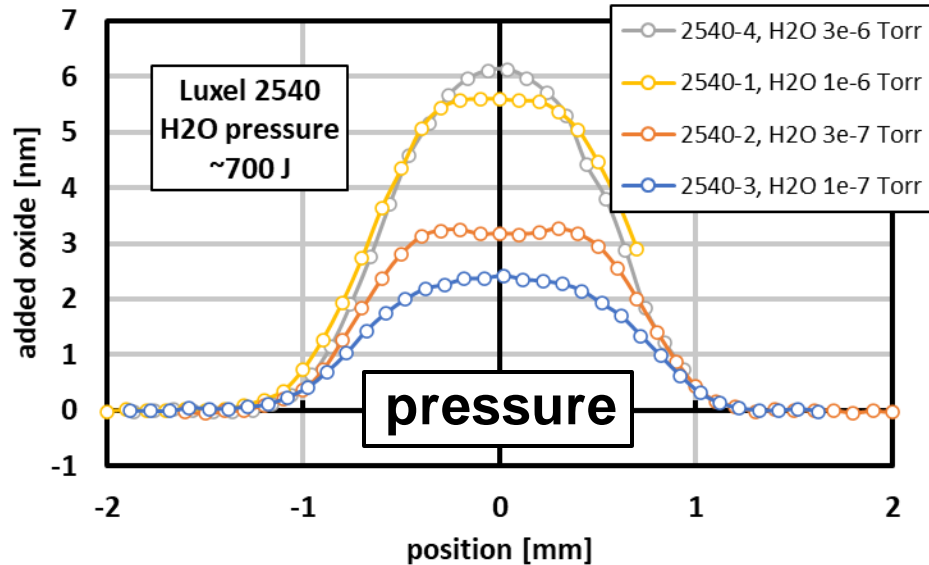
Al oxide growth

Variations of pressure, dose, and UV intensity

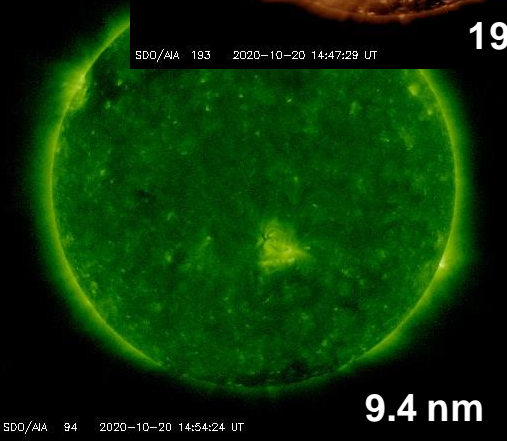
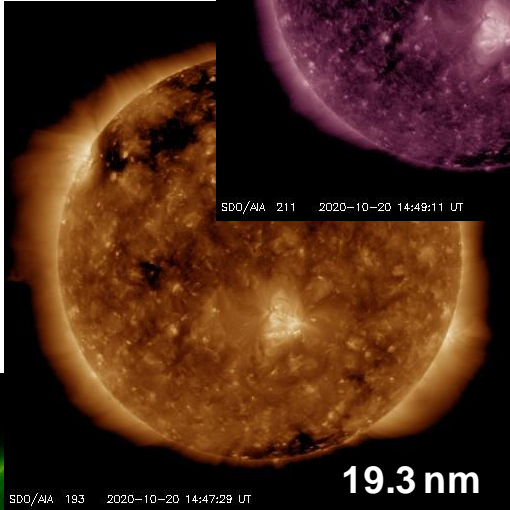
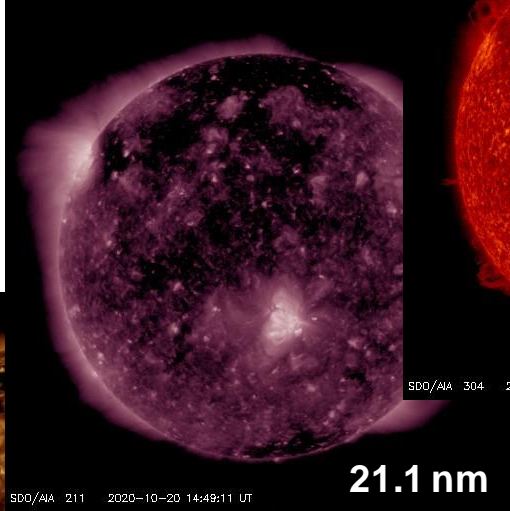
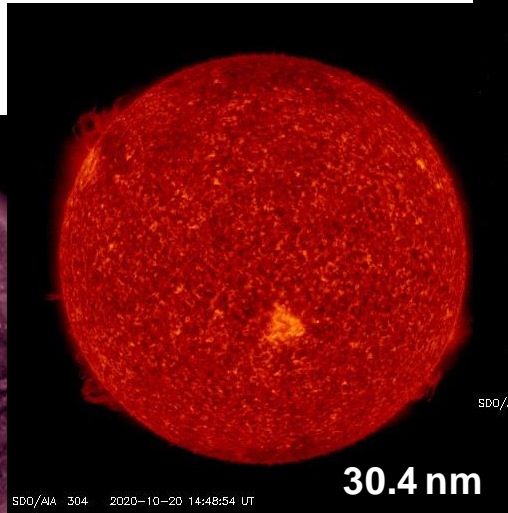
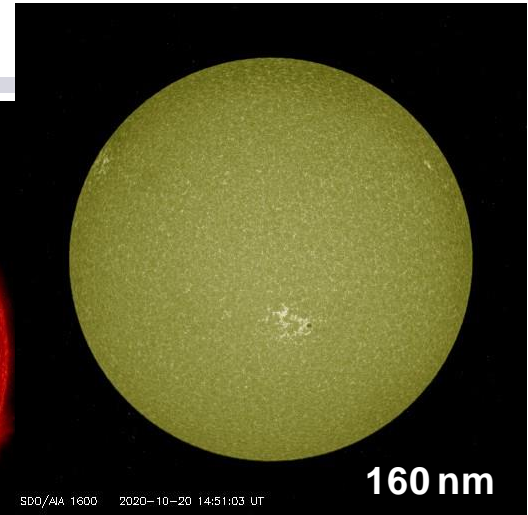
just the data



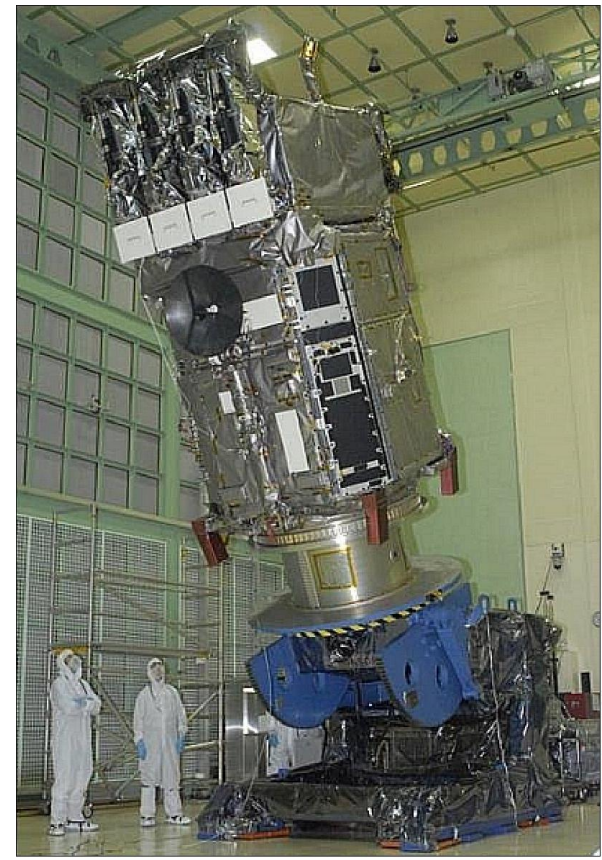
just the data



Motivation: Observing the sun



**Solar Dynamics Observatory
(SDO)
launched in 2010**



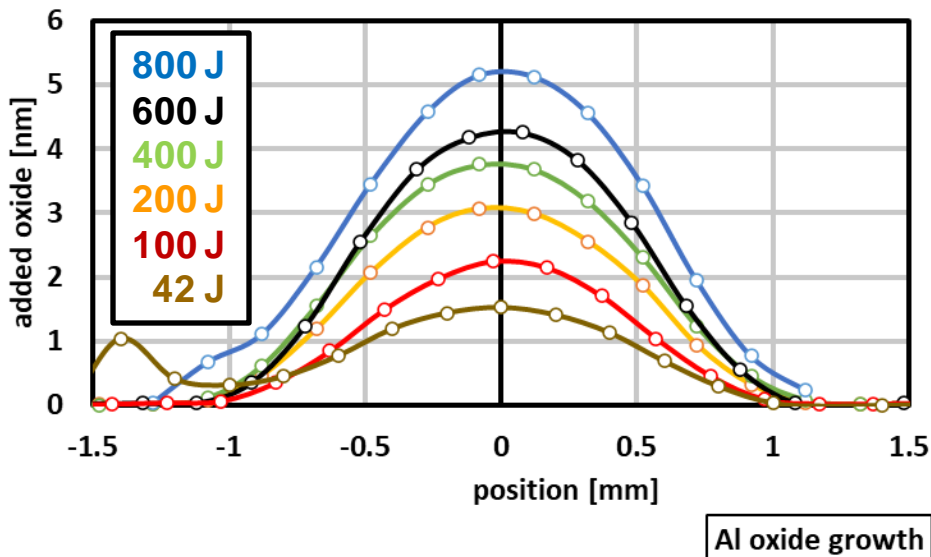
Model parameters

free parameters		value	expected		why expected
electron MF path	L	1.02	1.0 ± 0.2	nm	Schuermeyer (1968)
ion barrier hop energy	U_0	1.07	0.8 to 1.6	eV	literature
H ₂ O adsorption	$-U_1$	0.97	0.5 to 1.8	eV	crystal surface adsorption
OH ionization	$-U_2$	0.68	< 1.4	eV	OH electron affinity
H ₂ O / photon desorption yield	Y	4×10^{-4}	$< 30 \times 10^{-4}$		desorption from bulk H ₂ O

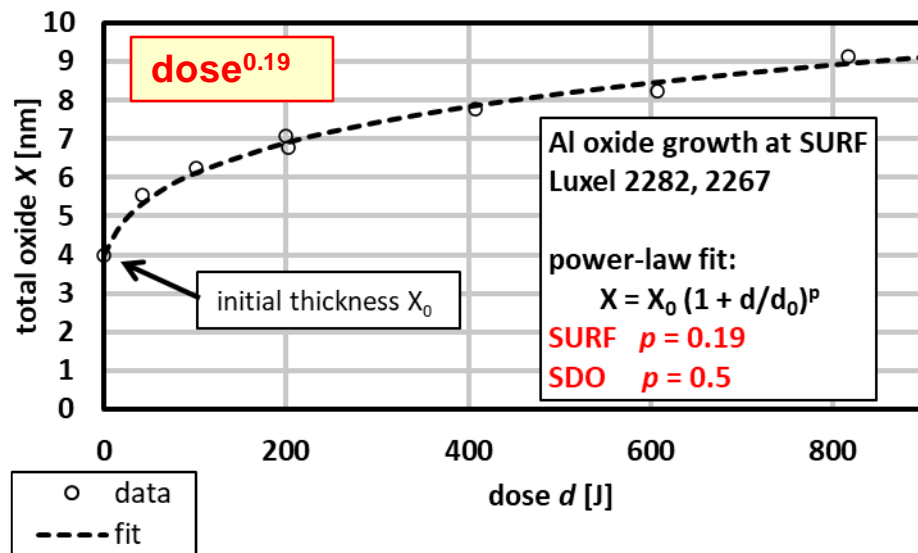
fixed parameters		value		why expected
initial thickness	X_0	4.	nm	NIST XPS & EDS, literature
phonon collision loss	E_{phonon}	0.05	eV	neutron scattering

Luxel 2282,2267: thickness vs dose

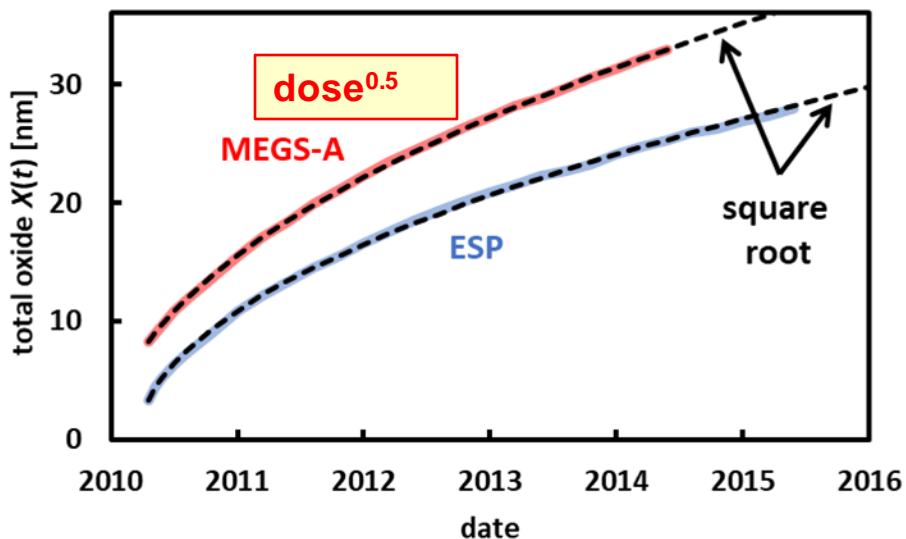
just the data



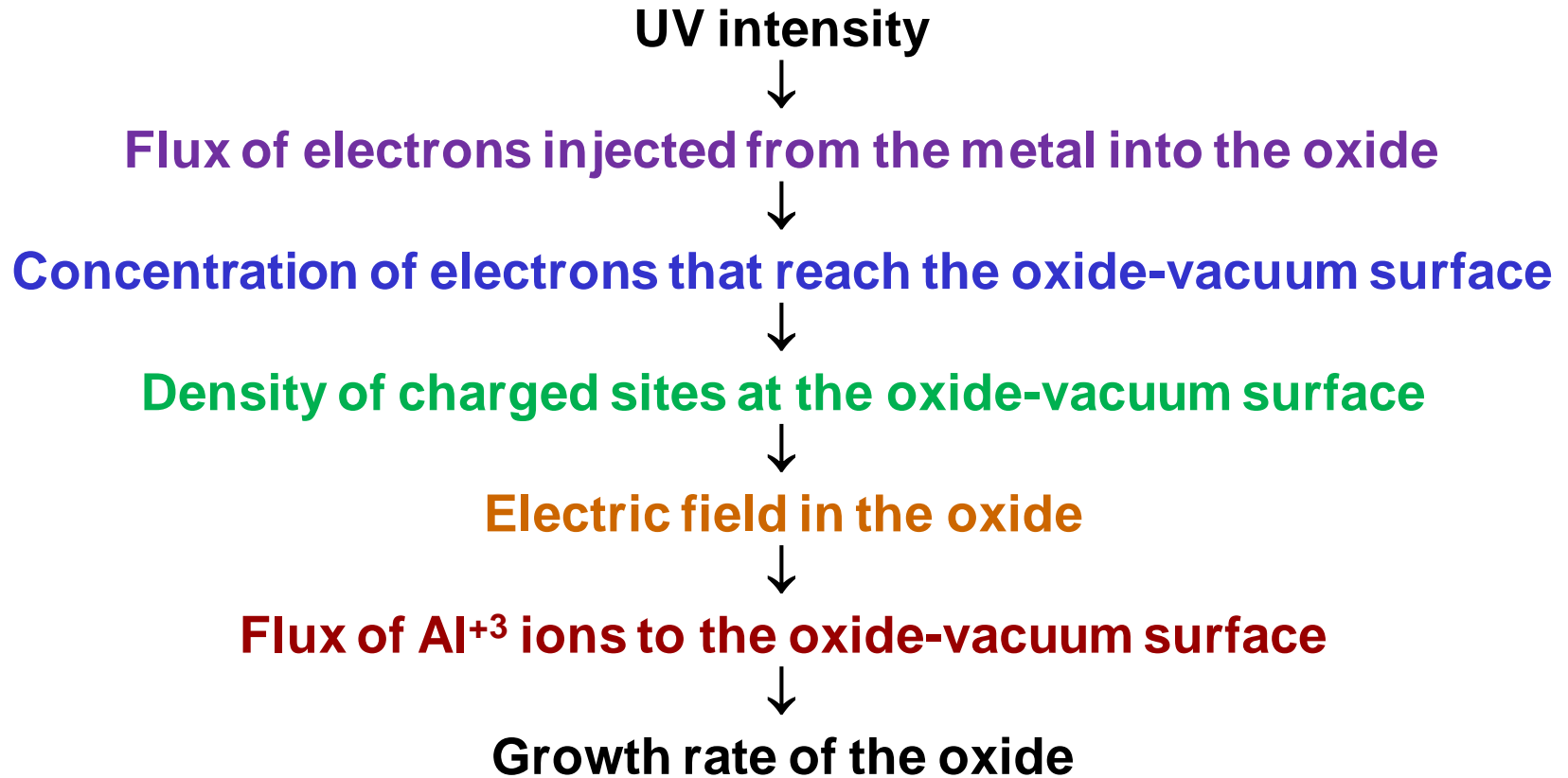
center oxide thickness vs UV dose



but... the SDO satellite is different



Steps in the model



Approximations in the model

One photon injects, at most, one primary photoelectron and no secondaries.

An electron-phonon collision occurs after the electron has traveled exactly one mean free path.

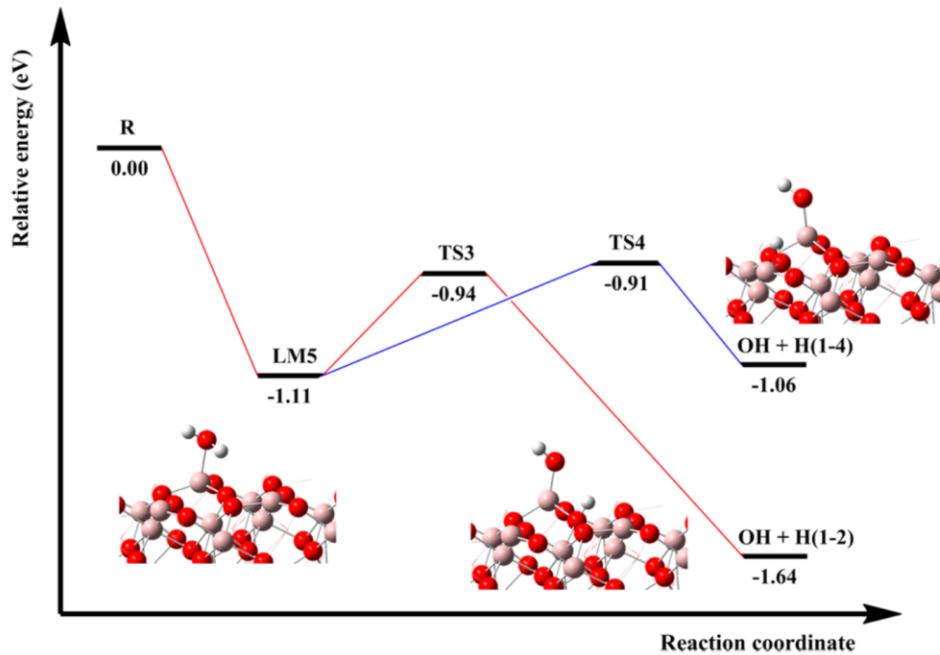
There is no space charge in the oxide.

The H₂O adsorption sites at the oxide-vacuum surface have a single energy, not a continuous distribution.

Except for the final reaction of Al⁺³ and OH⁻ ions, the chemical reactions at the oxide-vacuum surface are in equilibrium.

The oxide growth rate depends only on oxide thickness, H₂O pressure, and UV intensity, and not the history of these quantities.

Surface reactions: energy of adsorption U_1

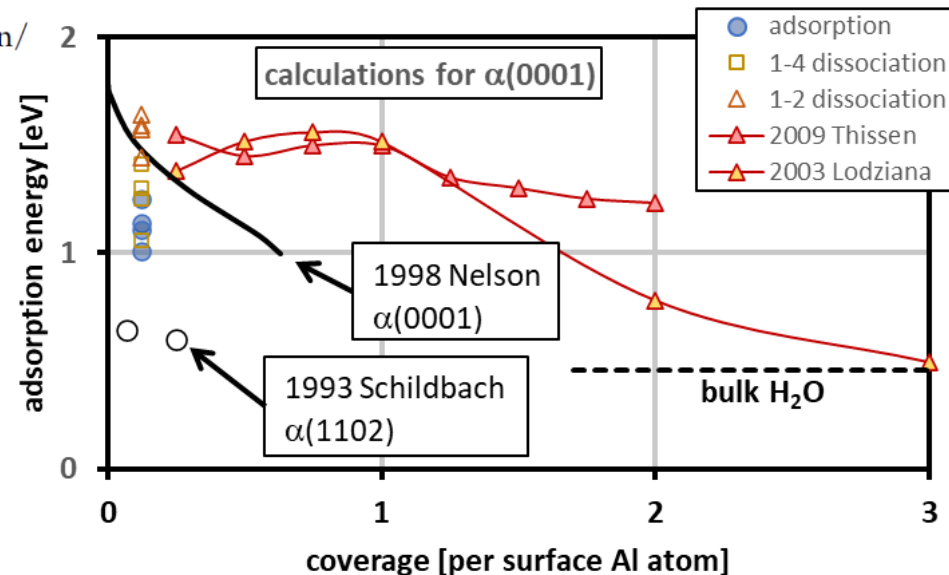


Use the same range measured on α -Al₂O₃(0001) by Nelson et al.

$$U_1 = -(1.4 \pm 0.4) \text{ eV}$$

Figure 8. Schematic potential energy profiles for H₂O adsorption/dissociation on the Al, O-terminated α -Al₂O₃(0001) surface.

2016 [Lu, Wu, Chen] H₂O adsorption-dissociation and H₂ generation by the reaction of H₂O with Al₂O₃ materials: A first-principles investigation



Surface reactions: energy of ionization U_2

Ionization and detachment of a hydroxyl group from an aluminum atom at the surface: $\text{Al}(\text{OH}) + e^- \rightarrow \text{Al} + \text{OH}^-$

The energy change is:

$$U_2 = (E_{\text{OH,ads}} - E_{\text{OH,dis}}) - A_{\text{OH}},$$

adsorption **dissociation from surface** **electron affinity**

Approximate the energy change for OH by that for H₂O:

$$E_{\text{OH,ads}} - E_{\text{OH,dis}} \approx E_{\text{H}_2\text{O,ads}} - E_{\text{H}_2\text{O,dis}} \cong 0.4 \text{ eV}$$

The energy change is then:

$$U_2 \approx 0.4 \text{ eV} - 1.8 \text{ eV} = -1.4 \text{ eV}$$

Electron scattering in the oxide

