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🔟 Robert F. Berg, ២ Charles Tarrio and Thomas B. Lucatorto









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Robert F. Berg,^{a)} (D) Charles Tarrio, (D) and Thomas B. Lucatorto

AFFILIATIONS

Sensor Science Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899

^{a)}Author to whom correspondence should be addressed: robert.berg@nist.gov

ABSTRACT

We present measurements and a model of aluminum oxidation induced by ultraviolet (UV) radiation. Spots of oxide were grown by focusing synchrotron radiation onto a polycrystalline aluminum membrane in the presence of water vapor at pressures from 3×10^{-8} to 1×10^{-4} mbar (3×10^{-6} to 1×10^{-2} Pa). The UV radiation passed through a sapphire (Al₂O₃) window, which ensured that the UV interacted with only the aluminum metal and not the oxide overlayer. The oxide profile of each spot was then determined by measuring the membrane's transmission at a wavelength of 17.5 nm. The model combined descriptions of photoemission from the Al metal, electron-phonon scattering in the oxide, Al³⁺ ion transport in the oxide, and the adsorption and ionization of H₂O on the oxide surface. It also accounted for UV-induced desorption of H₂O and the effect of the Al³⁺ ion flux on the surface reactions. The model's five free parameters were fit to the laboratory measurements of UV-induced oxidation. Then, using those values, the model was used to describe and understand the oxidation of similar aluminum membranes that were used to filter extreme ultraviolet on the Solar Dynamics Observatory, a sun-observing satellite. This understanding will help prevent similar problems on future satellites. These results are the first experimental confirmation of a model of UV-induced oxidation.

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I. INTRODUCTION

Most physical scientists know that aluminum does not "rust" because it is protected by a thin continuous layer of oxide. The oxide formation was explained in 1948 by Cabrera and Mott,¹ who showed that O^- ions on the oxide surface create an electric field that pulls Al^{3+} ions from the metal-oxide interface up to the oxide's outer surface, where they combine with the O^- ions. The oxide growth rate has an inverse exponential dependence on the oxide thickness, and Cabrera and Mott argued that the oxide grows until the electric field created by the Mott potential is too weak to move the Al^{3+} ions. In contrast, a recent study² showed that the limiting thickness occurs when the image charge seen by an O^- ion is too weak to keep it adsorbed. In either case, the electric field induced by the ions on the outer surface controls the oxidation rate.

The oxidation of any metal is complex because the oxide itself is a barrier between the metal and the oxidant. The case of aluminum at room temperature is simpler than most others because the amorphous oxide forms a tight seal with no cracks or grain boundaries, and, unlike at higher temperatures, the oxide growth is driven by the ion's electric mobility and not by its diffusivity. Even with these simplifications, there still exists the possibility of three fluxes: Al^{3+} ions, O^{-} ions, and electrons. The oxide inhibits these fluxes in different ways, but, if one ignores the electron emission from the oxide, the net charge transported must add to zero.

This work extends the theory of aluminum oxidation to include excitation by ultraviolet (UV) light. It was motivated by the puzzling behavior of two aluminum membranes that were used to filter the solar radiation seen by the Solar Dynamics Observatory (SDO) spacecraft.^{3,4} As shown in Fig. 1, over a period of five years the transmission of the filters degraded by a factor of 5. The unexpected degradation was initially blamed on carbon deposited on the filters by outgassed organic vapor. The light absorbed by a thin layer of carbon would have explained the degradation, but, as shown by Tarrio *et al.*,⁵ that was ruled out by the lack of degradation was caused by oxidation driven by outgassed water.⁶

Figure 2 shows the oxide thickness corresponding to the observed degradation. It is striking that the time dependence of the oxide thickness X(t) can be represented to within 0.3 nm by a





FIG. 1. Al filters used in two solar-viewing instruments on board the SDO satellite degraded during five years. MEGS-A = Multiple EUV Grating Spectrograph, ESP = EUV SpectroPhotometer.

simple square-root time dependence,

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

Here, *t* is the time, t_0 is a constant, and $X_0 = X(0)$ is the initial oxide thickness. This time dependence, known as "parabolic growth" in the corrosion literature, occurs when the temperature is sufficiently high to enable free diffusion of the ions across the oxide. However, the temperature on SDO was too low for such diffusion,⁷⁻¹⁰ and we will show that the oxide growth on SDO was limited instead by *electron* diffusion.

Understanding the degradation on SDO will help prevent similar problems on future satellites. This article describes how we reached that understanding by combining descriptions of photoemission, electron-phonon scattering, ion transport, and the adsorption and ionization of H_2O . We also took into account the



FIG. 2. Degradation of the Al filters on SDO (solid lines) corresponded to oxidation with the square-root time dependence of Eq. (1) (dashed lines).

UV-induced desorption of H_2O and the effect of the Al^{3+} ion flux on the surface reactions. Each of these concepts has been used in the literature in other contexts. What is new here, in addition to the measurements, is (1) modifying the concepts where needed, for example, by calculating an electron flux ratio instead of a concentration ratio, (2) simplifying the concepts by neglecting certain phenomena, such as space charge and ion diffusion, (3) combining the concepts, and (4) applying the combined model to the oxidant H_2O .

The free parameters in the resulting model were then fit to our laboratory measurements of UV-induced oxidation. (See Table I.) Finally, we show that the resulting model is consistent with the degradation on SDO. This result, and the fits to our laboratory measurements, are the first experimental confirmation of a model of UV-induced oxidation.

II. MODEL OF UV-INDUCED OXIDATION

A. Introduction

The first effort to understand UV-induced oxidation of metals was in 1947, when Cabrera *et al.*¹¹ exposed aluminum to the emission of a mercury discharge lamp filtered to remove long wavelengths. Cabrera¹² adapted the Cabrera–Mott model¹ to propose an explanation for the observed oxidation but, unfortunately, he made no quantitative comparison with the measurements. More recent work, especially by Ramanathan and co-workers^{13–17} and reviewed by Tsuchiya *et al.*,¹⁸ identified various phenomena associated with UV-induced oxidation, but there still has been no quantitative test of theory.

The present model starts with the Cabrera–Mott model as extended by Dignam and co-workers.^{19–21} That model described the creation of O^- ions by the adsorption and subsequent ionization of O_2 , and it then assumed that the density of electrons at the outer surface was determined by the electric field interacting with thermal electrons emitted from the metal into the oxide. The present model uses H₂O instead of O₂ as the oxidant, and it replaces the thermalized electrons with "hot" photoelectrons with energies much greater than kT. The key concepts, illustrated by Fig. 3, are as follows:

- 1. The UV causes "internal photoemission" that injects electrons from the metal into the oxide.
- 2. The injected electrons are scattered by phonons in the oxide, which reduces the electron flux that reaches the oxide-vacuum surface.
- 3. The electrons at the surface combine with adsorbed OH groups to create a surface charge composed of OH⁻ ions.
- 4. The surface charge creates an electric field in the oxide.
- The electric field causes Al³⁺ cations to move through the oxide and combine with OH⁻ ions at the surface, which grows more oxide.

Fortunately, the theory for each concept is well established. The challenge here was to identify which phenomena are important and to describe them as simply as possible. Phenomena that we considered to be less important include electron tunneling, details of the oxide band structure, and the formation of activated gas species such as ozone. The initial thickness was that of the native oxide. Its stability without UV illumination meant that **TABLE I.** Fixed and fitted oxide parameters in the model. Section II defines the parameters and Appendix D discusses the expected values. All uncertainties are standard uncertainties (coverage factor *k* = 1).

Quantity fixed		Value used	Expected	Why expected
Initial oxide thickness Al-Al ₂ O ₃ work function Electron-phonon collision loss	$egin{array}{c} X_0 \ oldsymbol{\phi} \ E_{ m op} \end{array}$	4.0 or 4.5 nm 2.6 eV 0.05 eV	(4 ± 1) nm (2.6 ± 0.6) eV (0.05 ± 0.01) eV	XPS and XRR of multiple surfaces Middle value of literature range Neutron scattering
Quantity fitted		Value fitted	Expected	Why expected
Electron mean free path Ion-hop barrier energy H ₂ O adsorption energy OH ionization energy H ₂ O/photon desorption yield	$L + U_0 - U_1 - U_2 Y$	$\begin{array}{l} (1.22\pm0.02) \text{ nm} \\ (1.07\pm0.02) \text{ eV} \\ (1.01\substack{+0.04\\-0.02}) \text{ eV} \\ (0.68\pm0.02) \text{ eV} \\ (4\pm1)\times10^{-4} \end{array}$	$\begin{array}{c} (1.0 \pm 0.2) \ \text{nm} \\ 0.8 - 1.6 \ \text{eV} \\ 0.5 - 1.8 \ \text{eV} \\ < 1.4 \ \text{eV} \\ < 18 \times 10^{-4} \end{array}$	Photoyield of biased Al-Al ₂ O ₃ -Au sandwich Oxidation at higher <i>T</i> by exposure to O ₂ Adsorption on crystal Al ₂ O ₃ OH electron affinity–H ₂ O dissociation energy Desorption from bulk H ₂ O

electron tunneling from the metal to the oxide surface was not significant.

In Secs. II B and II C, we describe how the electric field drives the flux of AI^{3+} ions, and then we show how to calculate that field.

B. Ion flux J_{AI}

The rate of growth of the oxide thickness *X* is the product of the Al ion flux J_{Al} and the volume a^3 of an Al₂O₃ unit,

$$\frac{dX}{dt} = a^3 J_{\rm Al}.$$
 (2)

See Fig. 4. Transition state theory^{21–24} leads to an equation of motion that describes the ion current J_{A1} when an electric field *F* is imposed across the oxide,

$$J_{\rm Al} = 2av \, \exp\left(-\frac{U_0}{kT}\right) \left[\sinh\left(\frac{qaF}{2kT} - \frac{a}{2}\frac{d}{dx}\right)n\right],\tag{3}$$

where

a is the size of an Al_2O_3 unit (m),

v is the ion escape attempt frequency (s^{-1}) ,

 U_0 is the activation energy for ion migration (J),



FIG. 3. Concepts in the model.

n is the concentration of mobile ions (m^{-3}) ,

q is the charge of the mobile ion (C),

k is the Boltzmann constant (J K^{-1}), and

T is the temperature (K).

Equation (3) ignores the energy required to move an Al ion from the metal to the oxide, and it assumes that the description of the periodic potential in a crystal is adequate also for an amorphous solid. Now, we make further assumptions:

- Ion diffusion is negligible.
- The electric field is due only to surface charges, i.e., space charge is negligible.
- The mobile species is Al^{3+} so that q = 3e.
- The concentration *n* of mobile ions is that of all the Al lattice atoms so that $n = 2/a^3$.
- The escape attempt frequency of a trapped ion is v = kT/h, where *h* is the Planck constant. This expression approximates the behavior of an ion of mass *m* near the top of the barrier between local minima. It is the number of states per unit length along the transition path (inverse de Broglie wavelength) multiplied by the average thermal speed,²²

$$v = \frac{(2\pi m kT)^{1/2}}{h} \left(\frac{kT}{2\pi m}\right)^{1/2} = \frac{kT}{h}.$$
 (4)



FIG. 4. Effect of an electric field F on a periodic lattice potential.



Equation (3) then becomes

$$\frac{dX}{dt} = \frac{4kTa}{h} \exp\left(-\frac{U_0}{kT}\right) \sinh\left(\frac{3eaF}{2kT}\right).$$
(5)

Obtaining the oxide growth rate requires knowledge of the electric field *F*.

C. Electric field F

Subsections II C 1–II C 6 describe in six steps how to calculate the surface charge and, thus, the electric field. The first four steps deal with the dimensionless quantities K_1p , which characterizes the adsorption of H₂O, and K_2 [e], which governs the ionization (electron attachment) of the adsorbed H₂O. The fifth step accounts for two phenomena that reduce the surface density of negative charge.

- Step 1: Identify the surface reactions and their equilibrium constants *K*₁ and *K*₂.
- Step 2: Estimate *K*₁*p* for dissociative adsorption of H₂O, where *p* is the H₂O pressure.
- Step 3: Estimate *K*₂[e] for ionization of OH, where [e] is the surface concentration of electrons.
- Step 4: Estimate $K_2[e]$ in terms of the injected photoelectron flux J_{e0} .
- Step 5: Account for the Al^{3+} ion flux and the UV-induced desorption of H_2O .
- Step 6: Solve for the electric field *F*.

1. Identify the surface reactions and their equilibrium constants K_1 and K_2

We start with Young and Dignam's description of oxidation by oxygen gas,²⁰ which assumes that the oxidation can be characterized by only two reaction steps. We first substitute H_2O as the oxidant, and later we include the effects of the Al^{3+} ion flux and UV-induced desorption.

The first reaction is the dissociative adsorption of an $\mathrm{H}_{2}\mathrm{O}$ molecule,

$$H_2O(gas) + open \rightleftharpoons OH|open|H.$$
 (6)

The form of the right side indicates that the initially unoccupied adsorption site, designated as *open*, is actually a pair of sites, one for the OH and one for the H. The two vertical lines correspond to the interfaces between the adsorption site and the adsorbate. Dissociation likely follows the adsorption of an H₂O molecule (theory^{25–30} and experiment^{31,32}), but it is not central to the present model. For the same reason, we ignore the fate of the hydrogen atoms, which might be incorporated interstitially into the oxide³³ or emitted as H₂.

Including dissociation explicitly in Eq. (6) allows the complex oxidation reaction to be characterized by only two reactions, the second being the ionization of OH. In equilibrium, the associated reaction equation is

$$\frac{d[OH]}{dt} = 0 = k_{1+}p[open] - k_{1-}[OH],$$
(7)

where k_{1+} and k_{1-} are the forward and backward rate constants, p is the H₂O gas pressure, and surface concentrations, with units m⁻², are denoted by bracket pairs []. (Later, in Sec. V, terms will be added for ionization, deionization, and UV-induced desorption). The associated equilibrium constant is the ratio

$$K_1 = \frac{k_{1+}}{k_{1-}}.$$
 (8)

The second reaction, driven by free electrons, is the ionization of the OH group,

$$OH|open|H + e^{-} \rightleftharpoons OH^{-}|open|H.$$
(9)

In equilibrium, the associated reaction equation is

$$\frac{d[\text{OH}^{-}]}{dt} = 0 = k_{2+}[e][\text{OH}] - k_{2-}[\text{OH}^{-}],$$
(10)

where k_{2+} and k_{2-} are the forward and backward rate constants and [e] is the concentration of free electrons at the surface. (Later, in Sec. V, terms will be added for UV-induced desorption and combination of the OH⁻ ions with Al³⁺ ions.) The associated equilibrium constant is

$$K_2 = \frac{k_{2+}}{k_{2-}}.$$
 (11)

Equations (7) and (10) for adsorption and ionization can be written as the equation pair,

$$K_1 p[open] - [OH] = 0,$$
 (12)

$$K_2[e][OH] - [OH^-] = 0,$$
 (13)

and the density of all surface sites can be related to that of the open sites by

$$[all] = [open] + [OH] + [OH^{-}].$$
 (14)

Solving these equations and using the estimate $[all] = a^{-2}$ for the density of all the surface sites yield the following expression for the coverage (dimensionless concentration) of surface ions:

$$\theta_{\text{OH}^-} \equiv \frac{[\text{OH}^-]}{[all]} = a^2 [\text{OH}^-] = \frac{K_1 p K_2[\text{e}]}{1 + K_1 p + K_1 p K_2[\text{e}]}.$$
 (15)

In the limit of low pressure, the surface ion concentration is proportional to both pressure and electron concentration,

$$\theta_{\mathrm{OH}^{-}} \cong K_1 p K_2[\mathbf{e}]. \tag{16}$$

In the limit of high electron concentration, the surface becomes saturated with ions and

$$\theta_{\mathrm{OH}^-} \cong 1.$$
 (17)



Equation (15) is similar to that obtained by Dignam and co-workers. It will be modified in a later step by accounting for the Al^{3+} ion flux and the UV-induced desorption of adsorbed OH and OH⁻.

2. Estimate K₁p for dissociative adsorption of H₂O

The values of k_{1+} and k_{1-} come from statistical mechanics and kinetic theory.^{20,35} The forward reaction rate is

$$k_{1+}p = (H_2O \text{ flux})(\text{effective } H_2O \text{ area}) = \frac{p}{(2\pi m_{H2O}kT)^{1/2}} \lambda_{H2O}^2,$$
(18)

where

$$\lambda_{\rm H2O} = \left(\frac{h^2}{2\pi m_{\rm H2O} kT}\right)^{1/2} \tag{19}$$

is the de Broglie thermal wavelength and $m_{\rm H2O}$ is the mass of an H₂O molecule. The backward reaction rate is

$$k_{1-} \cong (\text{attempt frequency})(\text{energy barrier}) = \frac{kT}{h} \exp\left(\frac{U_1}{kT}\right),$$
 (20)

where U_1 is the energy of adsorption. The backward rate is small because U_1 is negative.

Combining Eqs. (18) and (20) gives the dimensionless pressure

$$K_1 p = \frac{k_{1+}}{k_{1-}} p = \frac{p}{P'} \exp\left(\frac{-U_1}{kT}\right),$$
 (21)

where the characteristic pressure at 300 K is

$$P' = \frac{kT}{\lambda_{\rm H2O}^3} = 3.1 \times 10^{11} \,\text{Pa.}$$
(22)

3. Estimate K₂[e] for ionization of OH

The forward reaction rate is

$$k_{2+} = (\text{attempt frequency})(\text{effective electron area}) = \frac{kT}{h}\lambda_{e}^{2},$$
 (23)

where

$$\lambda_{\rm e} = \left(\frac{h^2}{2\pi m_{\rm e} kT}\right)^{1/2} \tag{24}$$

is the de Broglie thermal wavelength and $m_{\rm e}$ is the mass of an electron. The backward reaction rate is

$$k_{2-} \cong (\text{attempt frequency})(\text{energy barrier}) = \frac{kT}{h} \exp\left(\frac{U_2}{kT}\right),$$
 (25)

where U_2 is the energy of ionization. The backward rate is small because U_2 is negative.

Combining Eqs. (23) and (25) gives the dimensionless product

$$K_{2}[e] = \frac{k_{2+}}{k_{2-}}[e] = \lambda_{e}^{3} n_{e}(X) \exp\left(\frac{-U_{2}}{kT}\right),$$
(26)

where

$$n_{\rm e}(X) = \frac{[{\rm e}]}{\lambda_{\rm e}} \tag{27}$$

is the *volume* concentration of free electrons near the oxide-gas surface at position x = X.

4. Estimate $K_2[e]$ in terms of the injected photoelectron flux J_{e0}

The expression for $K_2[e]$ in Eq. (26) depends on the electron concentration $n_e(X)$ near the oxide-gas surface (specifically, the volume concentration, with units m⁻³). In the extended Cabrera-Mott model,^{19–21} Dignam and co-workers calculated $n_e(X)$ in two steps. First, they obtained the concentration $n_e(0)$ at the metaloxide surface. Then, they multiplied $n_e(0)$ by the ratio $n_e(X)/n_e(0)$ to obtain the concentration at the oxide-gas surface at x = X. The present model calculates instead the flux ratio J_{eX}/J_{e0} , where J_{eX} is the electron flux that reaches the oxide-vacuum surface at X and J_{e0} is the electron flux close to the metal-oxide boundary at 0.

As explained in Appendix A, applying Fermi–Dirac statistics to the free electron gas yields the energy distribution of photoelectrons injected into the oxide with energy *E*,

$$N(E) \equiv D(E)N_{\infty}(E) = D(E) \left(\frac{2}{\epsilon_F^2}\right) [I_0(E) - (\phi + E)I_1(E)], \quad (28)$$

where

E is the energy of the injected electrons (eV),

D(E) is the step function transmission coefficient at the metaloxide surface,

 $N_{\infty}(E)$ is the distribution of injected electrons if D(E) = 1 (eV⁻¹),

 $\boldsymbol{\epsilon}_F$ is the Fermi energy of aluminum (eV), and

 ϕ is the metal-oxide work function ($\phi_{Al-oxide}$) (eV).

The quantities I_0 and I_1 are integrals over UV wavelength λ defined as follows:

$$I_0(E) = \int_0^{\lambda_c} I'(\lambda) d\lambda \text{ and } I_1(E) = \int_0^{\lambda_c} \left(\frac{\lambda}{hc}\right) I'(\lambda) d\lambda.$$
(29)

Both integrands contain $I'(\lambda)$, the spectral intensity of the UV source, with units W m⁻² nm⁻¹. Both integrals depend on the electron energy *E* through the upper limit,

$$\lambda_c(E) \equiv \frac{hc}{(\phi + E)},\tag{30}$$

which is the longest wavelength that can inject an electron with energy $E \ge 0$ into the oxide. The special case E = 0 defines a JVSTA Journal of Vacuum Science & Technology A

characteristic UV intensity,

$$I_0(0) = \int_0^{\lambda_0} I'(\lambda) d\lambda \le I_0(E), \tag{31}$$

which is less than the total intensity if the source includes wavelengths longer than the photoemission cutoff at $\lambda_0 \equiv hc/\phi$.

Integrating Eq. (28) over all energies *E* yields the total flux of the injected electrons,

$$J_{e0} = \left(\frac{2}{\epsilon_F^2}\right) \int_0^\infty D(E) [I_0(E) - (\phi + E)I_1(E)] dE.$$
(32)

This can be written in terms of the characteristic UV intensity $I_0(0)$ as

$$J_{e0} \equiv \frac{I_0(0)}{E_0},$$
 (33)

where E_0 is the mean UV energy *absorbed* per injected electron. This is not to be confused with the mean energy $\langle E \rangle$ of the injected electrons, defined by

$$E = \frac{\int_0^\infty EN(E)dE}{\int_0^\infty N(E)dE}.$$
 (34)

The mean energy $\langle E \rangle$ is less than the absorbed energy E_0 because some of the electrons excited by the absorbed UV do not have enough energy to leave the metal.

The electrons injected into the oxide are scattered by collisions with defects, impurities, and phonons. The simplest model of the scattering is a 1D random walk, in which the electron changes direction randomly after traversing one mean free path *L*. In this context, the injected current J_{e0} first appears at a distance x = Lfrom the metal-oxide interface. At that location, the electron concentration is approximately the injected flux divided by the velocity,

$$n_{\rm e}(L) \simeq \int_0^\infty \frac{N(E)}{v(E)} dE \simeq \frac{J_{\rm e0}}{\left(2E/m_{\rm e}\right)^{1/2}}.$$
 (35)

The electron concentration near the oxide-vacuum surface (at x = X) has a similar form but with a flux that is smaller and a mean energy $\langle E_X \rangle$ that is between the thermal average and the initial mean energy $\langle E \rangle$ (at x = L),

$$\frac{3}{2}kT \leq \langle E_X \rangle \leq \langle E \rangle. \tag{36}$$

For the conditions typical of our experiments, Monte Carlo calculations found that the mean energy was closer to the upper bound of Eq. (36), namely,

$$\langle E_X \rangle \cong \langle E \rangle.$$
 (37)

We therefore expressed the electron concentration near the oxide-vacuum surface as

$$n_{\rm e}(X) \cong \frac{J_{\rm eX}}{\left(2E/m_{\rm e}\right)^{1/2}} = \frac{J_{\rm e0}}{\left(2E/m_{\rm e}\right)^{1/2}} g\left(\frac{X}{L}, F\right),$$
 (38)

where

$$g\left(\frac{X}{L}, F\right) \equiv \frac{J_{\text{ex}}}{J_{\text{e0}}}$$
 (39)

is the ratio of electron fluxes at the two oxide boundaries. That ratio depends on the thickness of the oxide X and the electric field F across it.

Using Eq. (38) in Eq. (26) gives the desired dimensionless electron concentration,

$$K_2[\mathbf{e}] \cong K_{20}g\left(\frac{X}{L}, F\right)\exp\left(\frac{-U_2}{kT}\right).$$
 (40)

The dimensionless constant K_{20} is proportional to the characteristic UV intensity $I_0(0)$. Using Eq. (33), one has

$$K_{20} = \frac{I_0(0)/E_0}{N_e(2\langle E \rangle/m_e)^{1/2}}.$$
(41)

We used the same approximation of Eq. (37) to describe the oxide growth on the SDO satellite even though its value of $\langle E_X \rangle$ was closer to the lower bound of Eq. (36). The associated concentration error was less than a factor of approximately

$$\left(\frac{2\langle E\rangle}{3kT}\right)^{1/2} = \left(\frac{2\ (0.59\ \text{eV})}{3\ (0.026\ \text{eV})}\right)^{1/2} \cong 4,\tag{42}$$

which corresponds to changing the value of the ionization energy U_2 by less than 0.04 eV. This bound is comparable to the fit uncertainty of 0.02 eV in Table I, and it is much smaller than the bound on U_2 discussed in Appendix D: $-U_2 < 1.4$ eV.

Figure 5 shows the results of Monte Carlo calculations of the normalized attenuation function defined by

$$f\left(\frac{X}{L},F\right) \equiv \frac{g(X/L,F)}{g(X/L,0)}.$$
(43)

This function focuses attention on the attenuation induced by the electric field. In the usual case, where $X \gg L$, the normalizing function in the denominator is

$$g\left(\frac{X}{L}, 0\right) \cong 1.32\left(\frac{L}{X}\right).$$
 (44)

The inverse *X* dependence is what one expects from diffusion with no electric field. The factor 1.32 occurs because the electrons are injected at only one mean free path above the metal surface, $x_{in} = L$.

The electrons lose their initial energy to collisions in the oxide, and eventually they become thermalized. The fate of a thermalized electron in the oxide depends on the strength of the



electric field. A strong field will sweep the electron back to the metal, which limits the oxide growth. For example, if the electrons have a maximum initial energy E_{max} and a mean free path L, and they lose energy E_{op} to an optical phonon at each collision, the maximum possible oxide thickness for the SURF (Synchrotron Ultraviolet Radiation Facility) exposures was

$$X_{\max} = L \left[1 + \left(\frac{E_{\max}}{E_{op}} \right) \right] \cong (1 \text{ nm}) \left[1 + \frac{(5 \text{ eV})}{(0.05 \text{ eV})} \right] = 101 \text{ nm}.$$

(45)

However, a thickness that recognizes the randomness of typical electron trajectories is much smaller,

$$X_{\text{typ}} \approx L \left(\frac{E_{\text{max}}}{E_{\text{op}}}\right)^{1/2} \approx (1 \text{ nm}) \left(\frac{5 \text{ eV}}{0.05 \text{ eV}}\right)^{1/2} = 10 \text{ nm}.$$
 (46)

In contrast, a weak field will allow the electrons to be scattered indefinitely by acoustic phonons. The electron transport is then simply diffusive, with an electron concentration in the oxide that decreases linearly with position x. A weak field is defined by

$$F \ll F_{\rm op} \equiv \frac{kT/e}{L} \approx \frac{(0.026 \,\text{eV})}{(1 \,\text{nm})} \approx 26 \,\text{MV}\,\text{m}^{-1},$$
 (47)

where L is the mean free path assumed for an electron interacting only with acoustic phonons.

The 1D random walk mentioned earlier did not adequately represent the weak-field behavior of the electron scattering, so a 2D random walk was used to obtain the results in Fig. 5. Appendix B describes the Monte Carlo calculation of f(F, X/L), and Appendix C



FIG. 5. Monte Carlo calculations of the attenuation function f(X/L, F), with mean free path L = 1.0 nm, for electric fields ranging from -1 to -900 MV m⁻¹. Approximate empirical descriptions (pastel curves) are overlaid on the data. The dashed line divides the strong-field and weak-field regions. The asymptotic value of 1 represents pure diffusion of the electrons.

explains how those results were characterized by empirical functions of F and X.

5. Account for the Al^{3+} ion flux and the UV-induced desorption of H_2O

Equation (10) for ionization is incomplete because it ignores the UV-induced desorption of OH^- ions, which is important at low pressure. It also ignores the Al^{3+} ion flux $J_{Al}(F)$, which irreversibly assimilates OH^- ions into the oxide. Including those terms gives

$$k_{2+}[e][OH] - k_{2-}[OH^{-}] - k_{uv}[OH^{-}] - \frac{3}{2}J_{Al} = 0,$$
 (48)

where k_{uv} is the rate constant for UV-induced desorption.

Equation (7) for adsorption also is incomplete because it ignores ionization, deionization, and UV-induced desorption. Including those terms gives

$$k_{1+}[open]p - k_{1-}[OH] - k_{uv}[OH] - k_{2+}[e][OH] + k_{2-}[OH^{-}] = 0,$$
(49)

where $k_{\rm uv}$ is the rate constant for UV-induced desorption of OH; for simplicity, it was assigned the same value as for OH⁻. Using Eq. (14) to describe [*open*] in terms of [*all*] and using Eq. (48) to describe the terms for ionization and deionization give

$$k_{1+}([all] - [OH] - [OH^{-}])p - k_{1-}[OH] - k_{uv}[OH] - k_{uv}[OH^{-}] - \frac{3}{2}J_{Al} = 0.$$
(50)



FIG. 6. Absorption spectrum of bulk H₂O compiled by Warren (Ref. 36) (left scale) compared to the spectral intensities of SURF (right) and the sun (right). The SURF spectrum, filtered through a sapphire window, overlaps that of H₂O only at wavelengths below 160 nm. The solar spectrum overlaps weakly at the Lyman-alpha line at 122 nm.



The coefficient that accounts for UV desorption is

$$k_{\rm uv} = J_{\rm UV} Y a^2. \tag{51}$$

Here, J_{uv} is a characteristic flux of UV photons from SURF, *a* is the size of an Al₂O₃ unit, and *Y* is the H₂O yield per *incident* (not absorbed) photon. The value of *J*uv for SURF was determined from the overlap of the SURF spectrum and the absorption spectrum of bulk water;³⁶ Fig. 6 shows that the overlap occurred only in the narrow range between the sapphire window's cutoff wavelength (145 nm) and the maximum wavelength of the H₂O absorption spectrum (160 nm). The value of J_{uv} for solar radiation was negligible because the only overlap between the UV solar spectrum and the H₂O absorption spectrum is at the Lyman-alpha line at 122 nm.

The value of the yield Y for SURF radiation on Al_2O_3 is uncertain. Öberg *et al.*³⁷ measured the yield Y caused by a hydrogen discharge lamp. They estimated the photon flux by assuming that the lamp's spectrum comprised the wavelength range 115– 170 nm, as measured by Muñoz Caro and Schutte.³⁸ The yield increased with the number of H₂O monolayers. In the limit of one monolayer, they found approximately

$$Y = 0.0012 \pm 0.0006.$$
(52)

This is an upper bound for Y because the yield for H_2O on Al_2O_3 , where it is adsorbed more strongly than on bulk H_2O , could be smaller. Therefore, Y was a free parameter in the fits.

6. Solve for the electric field F

We now multiply Eq. (48) by a^2/k_{2-} and Eq. (50) by a^2/k_{1-} to make them dimensionless and then combine them to eliminate the [OH] terms. The result is a single equation that relates the ion surface density [OH⁻] to the electron surface density [e] and the

 H_2O pressure p,

$$a^{2}[OH^{-}]\left[\left(1+\frac{k_{uv}}{k_{2-}}\right)\left(1+K_{1}p+\frac{k_{uv}}{k_{1-}}\right)+K_{1}pK_{2}[e]+K_{2}[e]\frac{k_{uv}}{k_{1-}}\right] -K_{1}pK_{2}[e]+\frac{3a^{2}}{2k_{2-}}J_{AI}\left(1+K_{1}p+\frac{k_{uv}}{k_{1-}}+K_{2}[e]\frac{k_{2-}}{k_{1-}}\right)=0.$$
(53)

To better understand and manipulate this expression, recall that the dimensionless products K_1p and $K_2[e]$ characterize, respectively, the adsorption and ionization of OH. Recall also from Eq. (5) that the dependence of the ion flux $J_{AI}(F)$ on F is

$$J_{\rm Al}(F) = J_{\rm a} \sinh\left(\frac{F}{F_a}\right),\tag{54}$$

where the amplitude is

$$J_{a} \equiv \frac{4kT}{ha^{2}} \exp\left(-\frac{U_{0}}{kT}\right),$$
(55)

and the characteristic field is

$$F_a = \frac{2kT}{3ea} = 49 \,\mathrm{MV} \,\mathrm{m}^{-1}.$$
 (56)

Next, define the dimensionless quantities,

$$\theta_{\mathrm{OH}^-} \equiv a^2 [\mathrm{OH}^-], \ c_a \equiv \frac{3}{2} \frac{a^2}{k_{2-}} J_a, \ \theta_a \equiv \frac{\varepsilon a^2}{e} F_a,$$
 (57)

where $\boldsymbol{\varepsilon}$ is the oxide dielectric constant, so that the ion flux function becomes

$$\frac{3a^2}{2k_{2-}}J_{\rm Al}(F) = c_{\rm a}\sinh\left(\frac{\theta_{\rm OH^-}}{\theta_a}\right).$$
(58)

Putting this description of $J_{Al}(F)$ into Eq. (53) expresses the surface coverage of surface ions as

$$\theta_{\rm OH^-} \equiv a^2 [\rm OH^-] = \frac{K_1 p K_2[e] - (1 + K_1 p + (k_{\rm uv}/k_{1-}) + K_2[e](k_{2-}/k_{1-})) c_{\rm a} \sinh(\theta_{\rm OH^-}/\theta_a)}{(1 + (k_{\rm uv}/k_{2-}))(1 + K_1 p + (k_{\rm uv}/k_{1-})) + K_1 p K_2[e] + K_2[e](k_{\rm uv}/k_{1-})}.$$
(59)

Due to the sinh function on the right-hand side, Eq. (59) must be solved numerically for θ_{OH-} . Once that is done, the oxide growth rate is obtained by using Eq. (2) and the "capacitor" equation that relates the electric field *F* to the surface charge density [OH⁻],

$$F = \frac{e[OH^{-}]}{\varepsilon}.$$
 (60)

Equation (59) can be compared with the approximate result of Eq. (15) by ignoring the UV-induced desorption terms to obtain

$$\theta_{\rm OH^-} \cong \frac{K_1 p K_2[e]}{1 + K_1 p + K_1 p K_2[e]} - \frac{1 + K_1 p + K_2[e] \frac{k_{2^-}}{k_{1^-}}}{1 + K_1 p + K_1 p K_2[e]} c_{\rm a} \sinh\left(\frac{\theta_{\rm OH^-}}{\theta_a}\right).$$
(61)



The first term is identical to Eq. (15). The second term, which originates from the last term of Eq. (48), accounts for the irreversible capture of OH^- ions by Al^{3+} ions. It is proportional to a ratio of polynomials that becomes unity in the limit of low electron concentration.

III. LABORATORY MEASUREMENTS

A. UV exposures

The exposures were carried out at the National Institute of Standards and Technology (NIST) on Beamline 1a³⁹ of the NIST Synchrotron Ultraviolet Radiation Facility storage ring (SURF III),⁴⁰ as shown in Fig. 7. A 1.5-m radius-of-curvature, Mo/Si multilayer-coated mirror collected radiation from SURF and focused it at the center of a cryopumped high-vacuum chamber with a base pressure of 1×10^{-8} mbar. The beam passed through a sapphire (Al₂O₃) window that prevented upstreaming of water vapor. It also limited the shortest wavelength to about 145 nm, which ensured that the UV interacted with only the aluminum metal and not the oxide overlayer. Exposures done with a BK7 window (310 nm wavelength cutoff) produced negligible oxidation. All exposures were done at room temperature.

The spectrum incident on the sample was the product of the SURF spectral irradiance, the mirror reflectance, and the sapphire window transmission. The SURF irradiance was calculated, and the sapphire window transmission was measured on SURF Beamline 3. The reflectance of the Mo/Si multilayer was calculated using an effective media approximation and our own optical constants.⁴¹ The resulting spectrum is shown in Fig. 8 along with the solar irradiance.

The samples were freestanding, polycrystalline, evaporated Al films, 250 nm thick and 10 mm in diameter, obtained from Luxel Corporation.⁴² For most of the results reported here, four spots were grown on each sample. Ultrahigh purity water was admitted through a leak valve, which was adjusted until the pressure monitored by an ionization gauge had stabilized at the desired value, somewhere from 3×10^{-8} to 1×10^{-4} mbar. The exposure to UV light was then



FIG. 7. Schematic of the Beamline 1a exposure facility.



FIG. 8. Irradiance falling on the filter in Beamline 1a (solid line, left-hand scale) and on the SDO spacecraft (dashed line, right-hand scale).

initiated. The incident power, which is proportional to beam current, was roughly 4.3 mW at the maximum beam current of 300 mA. During a typical exposure, the beam current cycled between 300 and 150 mA. The horizontal profile of the focal spot at Beamline 1a was approximately Gaussian with a full-width at half-maximum of 0.7 mm. The exposures lasted from 3 h to 20 days.

One sample was exposed for 8 days to oxygen at 2×10^{-6} mbar, a pressure typical of the H₂O exposures. The thickness of the added oxide was only 1.3 nm, much less than the 9 nm expected for H₂O at that pressure. However, it was approximately equal to that expected for the chamber's background H₂O pressure of 10^{-8} mbar.

B. Oxide thickness measurements

The oxide spots grown at Beamline 1a were characterized by measuring their transmission at 17.5 nm wavelength at Beamline $7.^{43}$ This wavelength is sensitive to the oxide thickness because it is absorbed more strongly by oxygen than by aluminum. The probe spot in Beamline 7 was sufficiently small to avoid blurring the measurements. The amount of oxygen measured by this method was converted to an oxide thickness by assuming that the oxide was composed of sapphire. It did not yield the oxide density, which has been of interest for electronic devices; see, for example, Ref. 18.

The transmission at 17.5 nm was measured as a function of position across the horizontal dimension of the oxide spot. These data were converted into relative transmission by dividing them by the transmission in an area well away from the spots. Finally, the oxide thickness added at each position was calculated using values for the optical constants of Al and Al_2O_3 from the CXRO tables.^{44,45} Some filters were measured also with electron-excited x-ray microanalysis with energy-dispersive x-ray spectroscopy (EDS) performed in a scanning electron microscope (SEM),^{6,46,47} which yielded similar results.

The reproducibility was approximately 0.3 nm. This was inferred from spots grown on different filters under the same



FIG. 9. 0.3 nm reproducibility of oxide growth was inferred from spots grown on different filters under the same conditions.

conditions. Figure 9 shows an example of spots grown on three filters, each with a fluence of 800 J while the H₂O pressure was 1.3×10^{-6} mbar. We attributed the variation among filters to differences in the physical structures of the filters, for example, differences in initial oxide thickness, grain size, or incorporated oxygen. It was unclear how these differences could cause a difference in peak shape (curved or flat top) as well as peak height. We did not expect the fitted oxide parameters U_0 , U_1 , U_2 , L, and Y to vary among the filters.

Details of the thickness measurement procedure can be found in Refs. 6 and 43.

IV. COMPARISON OF THE MODEL WITH LABORATORY MEASUREMENTS

The model was fit to the oxide thickness-versus-position curve for each spot by varying the five parameters U_0 , U_1 , U_2 , L, and Y. The other parameters were fixed as discussed in Appendix D. The fitting was done manually, which meant varying the parameter values, noting the agreement between the model and each of the spot profiles, and then iterating. The process was slow but robust against problems caused by the irreproducibility demonstrated by Fig. 9.

The figures in this section illustrate how the model was tested by comparing it with laboratory measurements that varied the H_2O pressure, the UV fluence, and the UV intensity. The final set of five values in Table I enabled the model to describe all the oxide spots to within approximately 20%.

Figure 10 shows the values of added oxide measured for four H_2O pressures and the corresponding calculated values. The dependence on pressure decreased with increasing pressure, and additional measurements taken at higher pressures, up to 10^{-4} mbar, found oxide thicknesses close to the maximum shown in Fig. 10. According to the model, this saturation with pressure occurred when the normalized surface density of adsorbed H_2O approached unity.

Figure 11 illustrates the effect of UV-induced photodesorption, which was strongest at our lowest H_2O pressure of



FIG. 10. Measured values (points) of added oxide and the corresponding calculated values (curves) for four H₂O pressures spanning a factor of 30.

 2.5×10^{-8} mbar. As discussed above, the maximum possible effect would have occurred if the H₂O/photon yield for desorption from Al₂O₃ had had the same value as that measured elsewhere³⁶ for desorption from ice, *Y* = 0.0012. The smaller value obtained here may have been due to the stronger binding energy of H₂O on Al₂O₃.

Figure 12 shows the values of oxide thickness measured across six spots and the corresponding curves calculated by the model. Each spot was grown with the same H₂O pressure of 1.3×10^{-6} mbar and the same average UV intensity, but their different exposure times resulted in fluences that spanned a factor of 20. The parameter values listed in Table I led to significant disagreement between the measured and calculated values. The disagreement was consistent with the 0.3 nm reproducibility mentioned in Sec. III. Increasing the value of the initial oxide thickness X₀ from 4.0 to 4.5 nm improved the agreement.



FIG. 11. UV-induced desorption was most important at the lowest pressure of 2.5×10^{-8} mbar. The upper and lower dashed curves show the effects of the minimum and maximum possible values of the H₂O/photon yield Y. The black curve is for the value Y = 0.004 that was fit to all the oxide spots. The points are the measured values.

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0

-1.5





0

0.5

1.5

1

-0.5

-1

Figure 13 shows the result of the longest exposure, which lasted 20 days. The top panel shows the SURF current. The incident power is proportional to the stored-beam current. In most runs, SURF was reinjected when the current dropped to half of its maximum of 300 mA. During the second half of this exposure, the beam was allowed to drop to very low values overnight and on weekends, when other beamlines were not operating. The modeled thickness-versus-position profile is approximately 1 nm above that of the measured data. We speculate that this difference occurred because the error of one or more of the model's approximations was larger at larger oxide thicknesses.

Figure 14 shows the results of two oxide spots that were grown with approximately the same UV fluence (203 and 227 J), the same H₂O pressure $(1.3 \times 10^{-6} \text{ mbar})$, but different UV intensities. Again, the SURF beam current is shown in the upper panel. The average UV intensity of the "slow" exposure was 1/12 that of the "normal" exposure. According to the model, the smaller growth of the normal exposure was due mainly to UV-induced desorption; removing desorption from the model by setting Y = 0 reduced the difference of the calculated peak heights from 1.4 to 0.3 nm.

Table I gives the final values of the eight oxide growth parameters. Five parameters were fit to the measurements, and three were fixed at literature values. One of the fixed parameters, X_0 , was varied in a narrow range after the free parameters had been chosen,



FIG. 13. The longest exposure lasted 20 days. UPPER: The UV intensity was proportional to the SURF beam current, which initially was kept within the usual limits. Later, the current was allowed to cycle to lower values, which decreased UV-induced desorption of H₂O. LOWER: The resulting measured values (points) and the corresponding calculated values (black curve).

with the constraint that the value of X_0 was the same for all four spots on a given filter. See Appendix D for a discussion about the expected values of the parameters.

The values of the five free parameters in Table I support the model's validity. Their fitted values are consistent with their expected values, and to within approximately 20% they enable the model to describe the thickness-versus-position profiles, not merely the peak amplitudes, of the 14 oxide spots shown above. The final deviations were attributed to the assumptions and approximations used in the model, and the uncertainties listed in Table I correspond to values that visibly increased those deviations. The upper bound of the adsorption energy U_1 was constrained only by the spot at the lowest pressure (Fig. 11); doubling the value of U_1 had little effect on the deviations of the other spots.

Table I gives the values of parameters that were fixed but depended on the spectral intensity of the UV source.

V. COMPARISON OF THE MODEL WITH THE SDO SATELLITE DEGRADATION

Figure 2 shows that the degradation seen in Fig. 1 corresponded to 24 nm of additional oxide for both SDO instruments.



FIG. 14. Two oxide spots were grown with approximately the same UV fluence, the same H_2O pressure, but different intensities. UPPER: The average UV intensity of the "slow" exposure was 1/12 that of the "normal" run. LOWER: The measured values (points) and calculated values (curves) for oxide thicknesses grown during two exposures of similar fluence. According to the model, the smaller growth of the normal exposure was due to UV-induced desorption.

We modeled that oxide growth by using the same values of the oxide parameters that were fit to the laboratory measurements (Table I). Other parameters, determined by the UV spectral intensity and listed in Table II, were fixed but differed from those of the laboratory measurements.

TABLE II. Fixed oxide growth parameters that depended on the UV spectral intensity. The energies are those of the photoelectrons immediately after injection into the oxide.

Quantity fixed		SURF	SDO
Mean UV energy per photoelectron Maximum	E_0	123 eV	1974 eV
photoelectron energy	E _{max}	5 eV	2 eV
Average photoelectron energy	$\langle E \rangle$	1.66 eV	0.59 eV
of desorption	$J_{\rm uv}$	$8.5 \times 10^{19} m^{-2} s^{-1}$	$1.3 \times 10^{15} \mathrm{m}^{-2} \mathrm{s}^{-1}$

TABLE III. Initial thickness X_0 and time constant t_0 fit to the empirical Eq. (1) and the temperature T and pressure p fit to the oxidation model for the two SDO instruments. All uncertainties are standard uncertainties (coverage factor k = 1).

	ESP	MEGS-A	Source
X_0 (nm)	3.4	8.3	Fit Eq. (1)
t_0 (year)	0.074	0.277	Fit Eq. (1)
T (K)	306 ± 1	314 ± 1	Fit model
p (mbar)	$(0.58 \pm 0.03) \times 10^{-8}$	$(1.5 \pm 0.10) \times 10^{-8}$	Fit model

The temperature T and H_2O pressure p were unknown, so they were made free parameters for both instruments. The temperature of each aluminum filter was a balance between the incoming solar irradiance and the outgoing radiation emitted to surrounding surfaces. The H_2O pressure at the filter was a balance between the outgassing of nearby surfaces and the vacuum conductance from the filter to the exterior of the spacecraft.

We set the values of X_0 to those in Table III, which were obtained by fitting the oxide growth versus time to the empirical Eq. (1). The value of X_0 for MEGS-A was twice the nominal value of 4 nm used to describe the SURF data; using the nominal value caused model deviations as large as 1.5 nm. The values of X_0 in Table III are consistent with Fig. 21 of Powell *et al.*;⁴⁸ they expected the native oxide thickness on a single side of a similar aluminum filter to increase with age from 1.8 nm to a maximum of approximately 7.5 nm.

The fits produced the values of *T* and *p* listed in Table III. The values of *T*, though reasonable, are not absolute; rather they reflect the temperatures on board SDO relative to the value of 300 K used to analyze the SURF exposures. The values of *p* are reasonable because they are consistent with the outgassing flux expected from SDO's thermal blankets.⁴⁹ Using these values of X_{0} , *T*, and *p*



FIG. 15. The solid lines are the oxide thicknesses inferred from the degradation of the SDO instruments MEGS-A and ESP. The dashed lines show the model calculated with the parameters in Table I, but with the values of the initial thickness X_0 taken from Table III.



reduced the rms fit deviations for both ESP and MEGS-A to less than 0.3 nm.

Figure 15 compares the model to the degradation of the SDO instruments. This agreement demonstrates that the model could describe the UV-induced oxide growth on board SDO as well as in the laboratory. The model also reproduced the square-root behavior one expects from diffusion [Eq. (1) and Fig. 2], with the diffusing entities being electrons and not ions.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Robert F. Berg: Conceptualization (equal); Formal analysis (lead); Writing – original draft (lead); Writing – review & editing (lead). **Charles Tarrio:** Conceptualization (equal); Investigation (lead); Writing – review & editing (supporting). **Thomas B. Lucatorto:** Conceptualization (equal); Formal analysis (supporting); Funding acquisition (lead); Project administration (lead); Writing – review & editing (supporting).

APPENDIX A: PHOTOELECTRONS INJECTED INTO THE OXIDE

The photoelectrons injected into the oxide have a broad energy distribution even if the photons are mono-energetic. This was first understood around 1930, when Fowler, Nordheim, and then DuBridge^{50–53} applied Fermi–Dirac statistics to the freeelectron gas. That theory agreed with contemporary measurements of the photoelectron energy distribution produced by photons with energies near threshold, namely, $hv \approx \phi$. It was also sufficient for the present purpose of aluminum illuminated by photons of energies 2 eV < hv < 9 eV. Further details, such as scattering of electrons in the metal, excitation of plasmons, and surface states were unnecessary (for example, see Refs. 54–61).

1. Monochromatic spectrum

The model of Fowler and DuBridge first derives the flux of electrons in the metal normal to the surface. Those electrons have a

velocity component v_x normal to the surface with a corresponding kinetic energy $\epsilon = (m/2)v_x^2$. The flux per unit energy [electrons/ (m² s eV)] is

$$n(\boldsymbol{\epsilon}) = \frac{4\pi m kT}{h^3} \ln \left[1 + \exp\left(\frac{\boldsymbol{\epsilon}_F - \boldsymbol{\epsilon}}{kT}\right) \right], \tag{A1}$$

where *m* is the electron mass and ϵ_F is the Fermi energy (chemical potential). The model then makes two assumptions. The first, as suggested by Fig. 16, is that an electron that leaves the metal has the energy

$$E = (\boldsymbol{\epsilon} + hv) - (\boldsymbol{\epsilon}_F + \boldsymbol{\phi}). \tag{A2}$$

In other words, the original energy ε is increased by the photon energy hv and then decreased by the potential step ϕ at the surface. Equation (A2) says that the photon adds energy to the normal direction only. This approximation is good for electrons with energies close to the threshold.⁵³ The second assumption is that the photocurrent is proportional to the number of electrons for which E > 0, namely, for which

$$\boldsymbol{\epsilon} + h\boldsymbol{v} > \boldsymbol{\epsilon}_F + \boldsymbol{\phi}. \tag{A3}$$

Then, in terms of the energies E of the *emitted* electrons, the flux per unit energy is

$$N_1(E) = \left(\frac{4\pi mkT}{h^3}\right) \ln\left[1 + \exp\left(\frac{h\nu - \phi - E}{kT}\right)\right].$$
 (A4)

The energy integral of this expression has no closed form, so it is fortunate that we will be able to use Eq. (A4) in the low-*T* limit, which is simpler,

$$N_1(E) = \left(\frac{4\pi m}{h^3}\right)(h\nu - \phi - E).$$
(A5)



FIG. 16. A photon increases the energy of an electron in the metal from ε to $\varepsilon + h\nu$. If the electron enters the oxide, its energy is $E = (\varepsilon + h\nu) - (\varepsilon_F + \phi)$.



2. Transmission at the metal-oxide surface

Not all of the electrons with sufficient energy (E > 0) enter the oxide because some are reflected at the metal-oxide interface. For a quantum particle of mass *m* and initial energy E_1 approaching a potential step E_{step} , the transmission coefficient is⁶²

$$D(E_1) = \frac{4k_1k_2}{(k_1 + k_2)^2},\tag{A6}$$

where

$$\hbar k_1 = \sqrt{2mE_1},\tag{A7}$$

$$\hbar k_2 = \sqrt{2m(E_1 - E_{\text{step}})}.$$
 (A8)

We will express k_1 and k_2 in terms of the final energy E of the emitted electron,

$$\hbar k_1 = \sqrt{2m(\boldsymbol{\epsilon} + h\boldsymbol{\nu})} = \sqrt{2m[E + (\boldsymbol{\epsilon}_F + \boldsymbol{\phi})]}, \qquad (A9)$$

$$\hbar k_2 = \sqrt{2m[(\boldsymbol{\epsilon} + h\boldsymbol{v}) - (\boldsymbol{\epsilon}_F + \boldsymbol{\phi})]} = \sqrt{2mE}.$$
 (A10)

Equations (A9) and (A10) show that $\varepsilon_{\rm F} + \phi$ is the only parameter needed to calculate the transmission coefficient *D*.

Figure 17 shows $D(\varepsilon)$ calculated for the transmission of electrons from aluminum into aluminum oxide, and Fig. 18 shows the effect of $D(\varepsilon)$ on the electron flux. The electron flux at energy ε is proportional to the product $D(\varepsilon)N(\varepsilon)$; see Eqs. (A5) and (A6). Figure 19 shows the effect of the approximation T = 0 K used in Eq. (A5); the integrated difference between the calculations at 300 and 0 K is a negligible fraction of the total integral.



FIG. 17. Transmission coefficient as a function of the energy ε of an electron in aluminum approaching the metal-oxide interface. In this example, $\varepsilon_{\rm F}$ = 11.7 eV is the aluminum Fermi energy, ϕ = 2.6 eV is the work function, and hv = 6.2 eV is the photon energy, so the step occurs at $\varepsilon_{\rm F}$ + ϕ – hv = 8.1 eV.



FIG. 18. Electrons in the aluminum have an energy distribution that is linear in energy ε . In this example, an electron must have an energy of at least $\varepsilon_{\rm F} + \phi - h\nu = 8.1 \,\text{eV}$, where $h\nu = 6.2 \,\text{eV}$ and $\phi = 2.6 \,\text{eV}$. The "transmitted" curve is the product $D(\varepsilon)n(\varepsilon)$. See Eqs. (A1) and (A6).

The flux that enters the oxide is the product

$$N(E) = D(E)N_1(E) = D(E)\left(\frac{4\pi m}{h^3}\right)(hv - \phi - E),$$
 (A11)

where the transmission coefficient D(E) is given by Eqs. (A6), (A9), and (A10).

3. Adequacy of the model of Fowler and DuBridge

Two pieces of evidence support Eq. (28), the simple description of the electron flux. The first is the work of Hechenblaikner *et al.*,⁶³ who measured the photoemission from gold surfaces induced by 5 eV photons. The model of Fowler and DuBridge described their data well. The second is the photoemission spectra of aluminum measured by Wooten *et al.*⁶⁴ We compared the simple monochromatic model to the energy distributions they measured with photon energies from 9.2 to 11.3 eV. After choosing an



FIG. 19. Close examination of Fig. 18 near $\varepsilon = \varepsilon_{\rm F}$ shows that the error caused by the approximation T = 0 K is negligible.



appropriate vertical scale, the calculation matched the energy dependence of the measured photoemission semi-quantitatively, to within roughly 20%.

4. Broad light spectrum

This section generalizes Eq. (A11) for a single photon energy to Eq. (28) for a broad light spectrum. Table IV summarizes the notation for the intensity functions used in the discussion.

Equation (A11) assumes that the light is monochromatic with energy hv and that every photon interacts with an electron. Generalize Eq. (A5) to light with a broad spectrum by weighting the single-frequency distribution $N_1(E)$ by the frequency-dependent photon intensity $I'_{\gamma\nu}(h\nu)$,

$$N_{\infty}(E) = \frac{1}{n_0} \int_{\phi+E}^{\infty} N_1(h\nu, E) I'_{\gamma\nu}(h\nu) d(h\nu).$$
(A12)

The lower limit of the integral is nonzero because the injected electron always has energy E > 0, and from Eq. (A2),

$$hv = (\phi + E) - (\epsilon_F - \epsilon) > \phi + E.$$
 (A13)

The normalization constant n_0 in Eq. (A12) is the flux of all electrons with energy ε normal to the surface. In the limit T = 0,

$$n_0 = \int_0^{\epsilon_F} n(\epsilon) d\epsilon = \left(\frac{4\pi m}{h^3}\right) \frac{\epsilon_F^2}{2}.$$
 (A14)

Using Eqs. (A5) and (A14) in (A12) gives

$$N_{\infty}(E) = \left(\frac{2}{\epsilon_F^2}\right) \int_{\phi+E}^{\infty} (h\nu - \phi - E) I'_{\gamma\nu}(h\nu) d(h\nu).$$
(A15)

Equation (A15) is written in terms of the photon flux per photon energy, $I'_{\gamma\nu}(h\nu)$, with units of (photon m⁻² s⁻¹ eV⁻¹), but we need it in terms of the energy flux per wavelength, $I'(\lambda)$, with units of (J m⁻² s⁻¹ nm⁻¹). To do so, use two mathematical relations, the first being

$$h\nu I'_{\gamma\nu}(h\nu) = \lambda I'_{\gamma\lambda}(\lambda),$$
 (A16)

where $I'_{\gamma\lambda}(\lambda)$ is the intensity per wavelength, with units of

TABLE IV. Notation for intensity functions.

	Spectral intensity		Total intensity
Photon flux per energy	$I_{\gamma \nu}'(h \nu)$	$\frac{\text{photon}}{\text{m}^2 \text{ s eV}} I_{\gamma} = \int_{0}^{\infty} I'_{\gamma\nu}(h\nu) d(h\nu)$	$\frac{photon}{m^2 \ s}$
Photon flux per wavelength	$I'_{\gamma\lambda}(\lambda)$	$rac{ ext{photon}}{ ext{m}^2 ext{ s nm}} I_{\gamma} = \int\limits_{0}^{\infty} I'_{\gamma\lambda}(\lambda) d\lambda$	$\frac{photon}{m^2 s}$
Energy flux per wavelength	$I'(\lambda)$	$\frac{\text{joule}}{\text{m}^2 \text{ s nm}} \qquad I = \int_0^\infty I'(\lambda) d\lambda$	joule m ² s



FIG. 20. Approximate descriptions of the irradiances of the sun (right vertical scale) and of SURF Beamline 1a (left scale) filtered by an Al_2O_3 (sapphire) window or a BK7 window. For SURF, the spot size was assumed to be 1 mm².

(photon $m^{-2} s^{-1} nm^{-1}$). The second relation is

$$I'_{\gamma\lambda}(\lambda) = \left(\frac{\lambda}{hc}\right)I'(\lambda).$$
 (A17)

With these two relations, Eq. (A15) becomes

$$N_{\infty}(E) = \frac{2}{\epsilon_F^2} [I_0(E) - (\phi + E)I_1(E)],$$
(A18)

where the two integrals are

$$I_0(E) \equiv \int_0^{\lambda_c} I'(\lambda) d\lambda, \qquad (A19)$$



FIG. 21. Energy distributions of injected electrons calculated for the sun (right vertical scale), for SURF Beamline 1a (left scale) filtered by an Al₂O₃ (sapphire) window or a BK7 window, and for monochromatic light with λ = 200 nm (left scale).

TABLE V. Total flux J_{e0} and mean energy $\langle E \rangle$ of electrons injected into the oxide
by the sun, by the solar Lyman-alpha line, and by SURF Beamline 1a (two window
materials). The assumed value of the metal-oxide work function was ϕ = 2.6 eV.

UV source	UV intensity $I_0(0)$ (J m ⁻² s ⁻¹)	Injected flux J_{e0} (electron m ⁻² s ⁻¹)	<i>E</i> ₀ (eV)	$\langle E \rangle$ (eV)
Lyman-alpha Sun SURF + BK7 SURF + Al ₂ O ₃	0.007 255 396 1660	$\begin{array}{c} 1.3 \times 10^{15} \\ 8.1 \times 10^{17} \\ 1.5 \times 10^{18} \\ 8.5 \times 10^{19} \end{array}$	33 1974 1638 123	2.87 0.59 0.44 1.66

and

$$I_1(E) \equiv \int_0^{\lambda_c} \left(\frac{\lambda}{hc}\right) I'(\lambda) d\lambda, \qquad (A20)$$

and the upper limit is

$$\lambda_c \equiv \frac{hc}{(\phi + E)}.\tag{A21}$$

Multiplying Eq. (A18) by the step transmission factor D and integrating over all energies E of the injected electrons yield Eq. (28) for the total electron flux.

5. Calculated energy distributions

Equation (A18) allows us to calculate the energy distributions of the injected electrons associated with the sun and with SURF Beamline 1a. Figure 20 shows the approximate irradiance descriptions used for the calculations shown in Fig. 21.

Figure 21 shows that the total electron flux into the oxide due to the sun is about 100 times smaller than that due to SURF. The SURF fluxes are similar to that due to a monochromatic irradiance of $I = 1000 \text{ m}^{-2}$ at an energy of 6.2 eV (1 mW mm⁻² at 200 nm wavelength). Figure 21 also explains why using a BK7 window caused negligible oxidation. Integrating the curves shown in Fig. 21 gives the values in Table V.

APPENDIX B: MONTE CARLO CALCULATION OF ELECTRON-PHONON SCATTERING

An electron moving through an amorphous oxide will be scattered by several types of interaction, and each type can be characterized by a mean free path. The Monte Carlo modeling of amorphous SiO₂ by Fitting and co-workers^{65–68} gives a guide to these types. They found that, at the low energies considered here, E < 6 eV, the dominant type was inelastic electron-phonon scattering, specifically the emission of optical phonons. Once the electron's energy *E* fell below that of the lowest optical phonon, $E < E_{op}$, the dominant type was elastic scattering by acoustic phonons. The electron's absorption of an optical phonon was possible but less likely.

The calculation for SiO_2 by Fitting and co-workers was more detailed than the present calculation for Al_2O_3 . It allowed for two

optical phonon modes, while the present calculation assumed only one. In the relevant range from 0.06 to 5 eV, they found that the mean free path for optical phonon events varied from 0.6 to 4 nm,^{67,68} while the present calculation assumed a constant effective value of $L \approx 1$ nm. Finally, Fitting and co-workers allowed the mean free path $L_{\rm ac}$ of acoustic phonon scattering to differ from $L_{\rm op}$, while the present calculation used the simplification $L = L_{\rm ac} = L_{\rm op}$.

Our Monte Carlo calculations comprised the following elements:

- Each electron was introduced at the location $x_{in} = L$, with an initial energy *E* that was systematically chosen from the photoemission distribution.
- The calculations were 2D. The electron's initial direction after a scattering event was characterized by the polar angle with respect to the *x*-axis, $-\pi/2 < \theta < +\pi/2$.
- A scattering event occurred when the electron had traveled one mean free path *L* since the previous event.
- For energies $E > E_{op}$, the event was inelastic because it caused the isotropic emission of one optical phonon. The electron had its energy decreased by $E_{op} = 0.05 \text{ eV}$,⁶⁹ and it was given a new random initial direction characterized by the polar angle θ . The mean free path *L* associated with optical phonons was approximated by a constant independent of energy.
- Once the energy fell below $E_{\rm op}$, the electron was thermalized by assigning it a random value of *E* from the Maxwell–Boltzmann distribution and a random value of θ . Thermalizing the electron at energies below $E_{\rm op}$ was justified by the near coincidence between $E_{\rm op} = 0.05$ eV and the thermal energy (3/2)kT = 0.04 eV.
- After being thermalized, the electron was assumed to interact only with acoustic phonons. The subsequent collisions were assumed to be elastic, and thus changed the electron's initial direction but not its energy. For simplicity, the mean free path $L_{\rm ac}$ associated with acoustic phonons was approximated by that for optical phonons, $L_{\rm ac} = L_{\rm op}$.

The input parameters were as follows:



FIG. 22. Energy distribution assumed for the photoelectrons injected into the oxide. The inset shows the flux with the maximum initial energy of 5.0 eV, as calculated by the trapezoidal rule.





FIG. 23. Each electron was injected at x = L and then moved ballistically until it had a collision, at which point it lost energy E_{op} and was given a new random direction. The electron was accelerated between collisions toward the metal by the electric field *F* in the oxide.

X, oxide thickness (nm) F, electric field in the oxide (MV/m) n_{max} , number of random electron trajectories $\phi_{oxide-vac}$, oxide-vacuum work function (eV) N(E), energy distribution of injected electrons (electron eV⁻¹) E_{op} , optical phonon energy loss per collision (eV) L, mean free path (nm)

The calculations began by injecting a hot electron with energy E at the location $x_{in} = L$, one mean free path away from the metaloxide surface. Figure 22 shows the energy distribution used to describe the photoelectrons injected during an SURF exposure. As described in Appendix A, the distribution was calculated by assuming that the SURF radiation of Beamline 1a was filtered through a sapphire window, and the Al–Al₂O₃ work function was 2.6 eV.

After the injection, the electron moved ballistically until it had a collision, at which point it lost energy E_{op} and was given a new random direction. As depicted in Fig. 23, the electron was accelerated between collisions toward the metal by the electric field *F* in the oxide. This process repeated until either the electron returned to the metal (x = 0), the electron reached the oxide-vacuum surface (x = X), or the electron's energy *E* fell below E_{op} . When $E < E_{op}$ occurred, the electron was thermalized, and its subsequent elastic collisions changed the electron's direction but not its energy. The path of a thermalized electron ended when it reached either x = 0or x = X.

APPENDIX C: DESCRIPTION OF THE MONTE CARLO RESULTS FOR F(X/L, F)

The Monte Carlo results were useful only after they were replaced by a function that could describe the normalized attenuation function f(X/L, F) for any value of electric field F and oxide thickness X. The following description comprises separate functions for strong and weak fields plus a transition function.

1. Strong field

A first step was discovering that, for each value of F, the strong-field data in Fig. 5 were well described by the *ad hoc* empirical function

$$f_{\text{strong}}\left(\frac{X}{L},F\right) \equiv \exp\left[c\exp\left(-\frac{a}{X/L}\right)\ln\left(1-\frac{X/L}{b}\right)\right],$$
 (C1)

where the constants *a*, *b*, and *c* were obtained by fitting Eq. (C1) to values of {(*X*/*L*), $\ln[f(X/L, F)]$ }. This form obeys the expected limits for X = 0 and $X = X_{max}$, where X_{max} is the maximum oxide thickness accessible to a hot electron. The exponential factor forces $f_{strong} = 1$ as $X \rightarrow 0$, and the logarithm factor is a singularity that corresponds to $f_{strong} = 0$ at X/L = b.

The values of *a*, *b*, and *c* depended on the value of *F*, and using Eq. (C1) to describe all the Monte Carlo results required finding expressions for those coefficients. Obtaining *b* in Eq. (C1) was aided by the understanding that, if one ignores the thermalized electrons, *b* is related to X_{max} in the 1D model approximately as follows:

$$b(F) \approx \frac{X_{\max}}{L} \cong 1 + \frac{E_{\max}}{E_{\text{op}} + eFL}.$$
 (C2)

Equation (C2) describes a "lucky" electron that, after being injected at $x_{in} = L$ with the maximum energy E_{max} , goes forward by one mean free path *L* with each collision, never backward. The energy cost of each advance is the emission of one optical phonon plus an increase *eFL* of the electric potential. The values of *b*(*F*) for large fields could be described approximately by

$$b(F) \cong 1 + \frac{E_{\max}}{E'_{\text{op}} + eFL'},\tag{C3}$$

where E'_{op} and L' were fitted values. The values of *a* and *c* in Eq. (C1) could then be approximated by linear functions of *b*,

$$a(F) \cong a_0 + a_1 b(F)$$
 and $c(F) \cong c_0 + c_1 b(F)$. (C4)

2. Weak field

The above descriptions of a, b, and c in Eq. (C1) worked for the stronger fields, but they failed for the weaker fields, defined approximately by

$$F \ll F_{\rm op} \equiv \frac{kT/e}{L} \approx \frac{(0.026 \,\text{eV})}{(1 \,\text{nm})} = 26 \,\text{MV}\,\text{m}^{-1},$$
 (C5)

where *L* is the mean free path. The failure occurred because a weak field cannot sweep every electron back to the metal, which allows more electrons to reach the oxide-vacuum surface. In the limit $F \rightarrow 0$, a thermalized electron will behave diffusively, and the attenuation function shown in Fig. 5 will approach $f(X/L, F) \rightarrow 1$.

To describe the weak-field behavior, we expressed f(X/L, F) as the parallel sum of two functions,

$$f_{\text{weak}}\left(\frac{X}{L},F\right) \equiv \left(\frac{1}{f_{\text{thin}}} + \frac{1}{f_{\text{thick}}}\right)^{-1},$$
 (C6)



where f_{thin} had the same form as that of f_{strong} in Eq. (C1), but with different coefficients,

$$f_{\rm thin}\left(\frac{X}{L},F\right) \equiv \exp\left[c_{\rm thin}\,\exp\left(-\frac{a_{\rm thin}}{X/L}\right)\,\ln\left(1-\frac{X/L}{b_{\rm thin}(F)}\right)\right].$$
 (C7)

Equation (C7) is valid for a thin oxide. It is the same as the strong-field expression of Eq. (C1) except that the values of a and c are independent of F and fixed at the zero-field limit of (C3) and (C4), namely,

$$a_{\text{thin}} \cong a_0 + a_1 b(0)$$
 and $c_{\text{thin}} \cong c_0 + c_1 b(0)$, (C8)

where

$$b(0) \equiv 1 + \frac{E_{\text{max}}}{E'_{\text{op}}} \tag{C9}$$

is Eq. (C3) at F = 0. The value of b_{thin} was approximately inversely proportional to F,

$$b_{\rm thin}(F) \cong \frac{F_{\rm b}}{F},$$
 (C10)

which is physically reasonable.

The form of f_{thick} was a straight line on the semilog plot of Fig. 5,

$$\ln\left[f_{\text{thick}}\left(\frac{X}{L},F\right)\right] \equiv -d(F)\frac{(X-X_d(F))}{L},\qquad(C11)$$

which is parametrized by the slope d and intercept X_d . Equation (C11) is valid for a thick oxide, for which $X \gg X_d$. It describes the steeper slope seen in Fig. 5 for curves at thicker oxide. The parameter d had an approximately linear dependence on the field F,

$$d(F) \cong d_0 + F/F_d,\tag{C12}$$

and the ratio X_d/L was approximately proportional to *b*. However, at small *b* (large *F*) the value of X_d/L seemed to saturate, and obtaining the necessary precision required a more complicated *ad hoc* description,

$$X_{\rm dL}(F) \equiv \frac{X_{\rm d}}{L} \cong X_{d00} + [X_{d0} + X_{d1}b(F)] \left[1 - \exp\left(-\frac{b(F)}{b_{Xd}}\right)\right]^4.$$
(C13)

The border between weak and strong fields is the transition field F_0 defined by the equality

$$f_{\text{strong}}\left(\frac{X}{L}, F_0\right) \equiv f_{\text{weak}}\left(\frac{X}{L}, F_0\right).$$
 (C14)

In the approximation that

$$a(F_0) \cong a_0 + a_1 b(0)$$
 and $c(F_0) \cong c_0 + c_1 b(0)$, (C15)

this is equivalent to

$$b(F_0) = b_{\text{thin}}(F_0) \tag{C16}$$

or

$$1 + \frac{E_{\max}}{E'_{op} + eF_0L'} = \frac{F_b}{F},$$
 (C17)

where E'_{op} and L' are the fitted values of Eq. (C3), Solving for F_0 leads to an approximate expression for the transition field,

$$F_0 \simeq \frac{E'_{\rm op}F_{\rm b}}{E_{\rm max} + E'_{\rm op} - eLF_{\rm b}}.$$
 (C18)

For a mean free path of 1 nm, the SURF exposures would have had $F_0 = 4.7$ MV/m.

3. All fields

The strong-field and weak-field expressions, Eqs. (C1) and (C5), were combined as a parallel sum

$$f_{\rm emp}\left(\frac{X}{L},F\right) \equiv \left(\frac{1}{f_{\rm any}} + \frac{K_{\rm trans}}{f_{\rm thick}}\right)^{-1},$$
 (C19)

where f_{any} was defined similarly to f_{strong} ,

$$f_{\rm any}\left(\frac{X}{L},F\right) \equiv \exp\left[c_{\rm any}\,\exp\left(-\frac{a_{\rm any}}{X/L}\right)\,\ln\left(1-\frac{X/L}{b_{\rm any}}\right)\right],$$
 (C20)

but with coefficients that were appropriate for any electric field F,

$$a_{\rm any} \equiv \min(a, a_{\rm thin}), \tag{C21}$$

$$b_{any} \equiv \max(b, b_{thin}),$$
 (C22)

$$c_{\text{any}} \equiv \min(c, c_{\text{thin}}).$$
 (C23)

The *ad hoc* transition function K_{trans} in Eq. (C19) decreases rapidly from 1 to 0 as the field *F* increases above the transition field F_0 . It was defined so that the contribution of f_{thick} was significant only at small fields,

$$K_{\text{trans}} \equiv \frac{1}{2} \left(1 + \tanh\left[4\left(1 - \frac{F}{F_0}\right)\right] \right). \tag{C24}$$

Table VI lists the parameters that were fitted to Eqs. (C3), (C4), (C10), (C12), and (C13). The calculations for the SURF spectrum were performed for two values of the mean free path L, and the resulting fitted values were approximately independent of L. The values in Table VI reflect small adjustments that made the independence exact. Figure 5 illustrates the adequacy of the description.

TABLE VI. Parameters used to describe the Monte Carlo calculation results. The				
calculations used the work function value $\phi = 2.6 \text{ eV}$ and the photon energy				
$E_{op} = 0.05 \text{ eV}$. Two values of the mean free path were used, $L = 0.5 \text{ nm}$ and				
L = 1.0 nm; the resulting parameters are independent of L.				

Strong field		SURF		Sun	
E_0 (eV)		5.0		2.0	
$E'_{\rm op}/E_{\rm op}$	$L'_{\rm op}/L_{\rm op}$	2.092	0.912	1.304	0.912
a_0	a_1	0.00	0.18	0.27	0.13
c_0	c_1	3.2	0.37	3.1	0.59
$LF_{\rm b}~({\rm eV})$		0.24		0.24	
Transition					
LF_0 (eV)		0.004 72		0.007 36	
Weak field					
d_0	$F_{\rm d}$ [MV/m]	0.45	25.0	0.75	25.0
X_{d0}	X_{d1}	0.00	0.14	0.00	0.13
X _{d00}	$b_{ m Xd}$	9	50	6	50

APPENDIX D: PARAMETERS IN THE MODEL

This appendix gives more information about the values in Table I.

1. Initial oxide thickness X₀

Evertsson *et al.*⁷⁰ used x-ray reflectivity (XRR) and x-ray photoelectron spectroscopy (XPS) to measure the native oxide thickness on two Al crystal surfaces and four Al alloy surfaces. With only one exception, their results fell in the range $X_0 = (4 \pm 1)$ nm. EDS measurements made on several of our samples⁶ found $X_0 = (4.0 \pm 0.5)$ nm. However, we note that Powell *et al.*⁴⁸ gave examples of similar aluminum filters with a single-side value as large as $X_0 = 7.5$ nm.

2. Al-Al₂O₃ work function ϕ

This work function is the difference between the Fermi level of Al and the bottom of the Al₂O₃ conduction band. It was measured several times by groups using photoelectron spectroscopy on metal-insulator-metal structures. Kadlec and Gundlach⁷¹ found that ϕ increased from 1.9 to 2.4 eV as the oxide thickness increased from 2.9 to 5.5 nm. Afanas'ev and Stesmans⁷² reviewed literature values for ϕ and found values from 2.0 to 3.2 eV, depending on the oxide growth temperature; a higher temperature gave a larger work function. Xu *et al.*⁷³ found values from 2.3 to 2.9 eV, depending on postdeposition annealing. These ranges can be described approximately by

$$\phi \approx (2.6 \pm 0.6) \,\mathrm{eV}.\tag{D1}$$

There is some discussion in the literature^{71,74,75} that electron scattering in the oxide can lead to an overestimate of ϕ , but the effect is typically only about 0.2 eV.

The work function can also be estimated by the difference⁷²

$$\phi \approx \phi_{\rm Al-vac} - A_{\rm oxide},$$
 (D2)

where f_{Al-vac} is the work function for bare aluminum and A_{oxide} is the electron affinity of Al₂O₃.

The value of ϕ_{Al-vac} was measured by Eastment and Mee⁷⁶ on the (111), (100), and (110) faces of bare aluminum; they found the average value $\phi_{Al-vac} = (4.2 \pm 0.1)$ eV. Grepstad *et al.*⁷⁷ found the similar average value $\phi_{Al-vac} = (4.3 \pm 0.1)$ eV. Alimardani and Conley⁷⁸ used a scanning Kelvin probe to measure the work function of Al in air and obtained $\phi_{Al-vac} = 4.2$ eV. Feuerbacher and Fitton⁷⁹ found ϕ_{Al-} vac = (4.0 ± 0.6) eV for samples that had an oxide layer due to several days' exposure to ambient atmosphere; the uncertainty reflects the scatter among multiple samples. The value of Feuerbacher and Fitton, though consistent with the measurements on bare aluminum, may have been due to water exposure, which can lower the work function by as much as 1.0 eV.⁸⁰ We adopted the value $\phi_{Al-vac} = (4.25 \pm 0.15)$ eV.

The electron affinity A_{oxide} was measured by Shlyakhov *et al.*⁸¹ using internal photoemission; they found $A_{\text{oxide}} = (1.9 \pm 0.1)$ eV, where the uncertainty is typical of the quantities from which they derived A_{oxide} . For comparison, the electron affinity of an oxygen atom is $A_{\text{O}} = 1.46$ eV.⁸²

Using the above values for ϕ_{Al-vac} and A_{oxide} in Eq. (D2) gives

$$\phi \approx (4.25 \pm 0.15) - (1.9 \pm 0.1) \,\mathrm{eV} = (2.4 \pm 0.2) \,\mathrm{eV},$$
 (D3)

which is consistent with Eq. (D1).

3. Mean free path L

The fitted value is consistent with the value $L = (1.0 \pm 0.2)$ nm obtained by Schuermeyer *et al.*;⁸³ they compared their Monte Carlo calculations to their measurements of photocurrents through Al₂O₃ films, across which they applied various bias voltages.

4. AI_2O_3 barrier to AI^{+3} ion transport U_0

Table VII lists several studies that characterized the temperature dependence of oxide growth by the factor $\exp[-U_0/(kT)]$, where U_0 is the height of the barrier between ion sites within the

TABLE VII. Measured values of the barrier U_0 to ion transport in Al₂O₃. The uncertainties of Refs. 84 and 85 were estimated from the scatter of their data.

Study	Method	Temperature (K)	Pressure (Pa)	U_0 (eV)
1966 Harkness ⁸⁶	Anodization,			
	180 V	273-298		1.30 ± 0.15
1966 Dignam ⁸⁴	O ₂ exposure	523-723	1300	1.6 ± 0.1
1981 Hayden ⁸⁷	O ₂ exposure	600-800	0.013	1.17 ± 0.05
1982 Grimblot ⁸⁵	O ₂ exposure	300-600	$(3-40) \times 10^3$	0.9 ± 0.1
2008 Reichel ⁸⁸	O ₂ exposure	350-600	0.0001	1.1 ± 0.1
2021 Gorobez ⁸⁹	O ₂ exposure	300-600	1000	0.12 ± 0.02





FIG. 24. Four literature values of U_0 plotted as a function of (arbitrarily) oxidant pressure.

oxide. Based on the subset shown in Fig. 24, we adopted the expected range $U_0 = (1.2 \pm 0.4)$ eV.

5. H₂O adsorption energy U₁

Figure 25 shows that literature values for the adsorption energy U_1 of H₂O on Al₂O₃ span a broad range. Most of the points are calculations made for various surfaces, including those named adsorption, 1–4 dissociation, or 1–2 dissociation.^{25–30} Calculations by Thissen *et al.*²⁷ and Lodziana *et al.*³⁰ span a large range of H₂O coverage. The experimental points include the LTIR measurements of Nelson *et al.*³² on the crystal surface α -Al₂O₃(0001), which had an unexpected dependence on coverage. Also shown are the TPD values measured by Schildbach and Hamza⁹⁰ on the surface a(1102). For coverages less than 1, the experimental values are



FIG. 25. Literature values for the adsorption energy U_1 span a broad range. The values of Nelson *et al.* (Ref. 32) and Schildbach and Hamza (Ref. 90) are measurements, and the others (Refs. 25–30) are calculations made for various surfaces. The present work assumed a single value for U_1 even though the H₂O pressures used corresponded to coverages from 0.02 to 0.92.

described by

$$U_1 = -(1.2 \pm 0.6) \,\mathrm{eV}.$$
 (D4)

6. OH ionization energy U₂

The model assumes that a free electron promotes oxidation by the ionization and detachment of a hydroxyl group from an aluminum atom at the surface,

$$Al(OH) + e^- \rightarrow Al + OH^-.$$
 (D5)

An estimate of the associated energy change is

$$E_{\text{OH}^-} = (E_{\text{OH},\text{ads}} - E_{\text{OH},\text{dis}}) - A_{\text{OH}},$$
 (D6)

where $E_{OH,ads}$ and $E_{OH,dis}$ are the energies for the adsorption and dissociation of the neutral OH radical on the oxide and A_{OH} is the electron affinity for OH.⁹¹ We can approximate the difference for the OH radical by that for the H₂O molecule (see references in the section on U_1),

$$E_{\text{OH,ads}} - E_{\text{OH,dis}} \approx E_{\text{H2O,ads}} - E_{\text{H2O,dis}} \cong 0.4 \,\text{eV}.$$
 (D7)

The energy change is then bounded by

$$U_2 < E_{\text{OH}^-} \approx 0.4 - 1.8 \,\text{eV} = -1.4 \,\text{eV}.$$
 (D8)

The negative value means the reaction is energetically favored.

7. Miscellaneous characteristics of Al₂O₃

a. Unit size a

The molar mass of Al₂O₃ is $M = 0.102 \text{ kg mol}^{-1}$ and the density of polycrystalline aluminum oxide is $\rho = 3984 \text{ kg m}^{-3}$, ⁹² so the average unit spacing is $a = [M/(N_A \rho)]^{1/3} = 0.35 \text{ nm}$, where N_A is Avogadro's number.

b. Relative dielectric constant $\varepsilon/\varepsilon_0$

The relative dielectric constant of crystalline Al₂O₃ (sapphire) varies from 8.9 to 11.1, depending on the orientation.⁹³ Amorphous oxide films typically have lower values due to their increased porosity and possible incorporation of OH groups. Film grown by ALD (atomic layer deposition) had values of 7.6 ± 0.3 ,⁹⁴ 7.2 ± 0.3 ,⁹⁵ and 7.6.⁹⁶ Not knowing how our commercial samples were fabricated, we adopted the value $\varepsilon/\varepsilon_0 = 8 \pm 1$ or $\varepsilon = 7 \times 10^{-11}$ F m⁻¹.

c. Bandgap E_{gap}

The 1990 review by French⁹⁷ assigns $E_{gap} = 8.8 \text{ eV}$. However, a 2007 calculation for α -Al₂O₃ by Sevik and Bulutay⁹⁸ found 6.2 eV, and recent measurements on amorphous Al₂O₃ by Afanas'ev *et al.*,⁹⁹ Xu *et al.*,⁷³ and Filatova and Konashuk¹⁰⁰ found, respectively, 6.2, 6.2, and 7.0 eV, all with uncertainties of ~0.1 eV. Given this spread of results and assuming that our oxide samples are amorphous, we adopted $E_{gap} = (6.6 \pm 0.4) \text{ eV}$.



DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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