Prediction of Schottky Barriers at Electrified Junctions

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We consider the electronic barriers that develop at the surface of a semiconductor connected to an electrode or immersed in an electrolyte. These barriers govern the current-rectifying ability of photodiodes and the light-harvesting efficiency of photoelectrodes. A model that accounts for the alignment of the donor and acceptor levels across the junction enables us to predict the heights of the barriers as a function of the donor–acceptor offsets, including the effects of charge trapping and Fermi-level pinning. This model provides a first-principles basis to previous empirical descriptions of semiconducting junctions under bias, with far-reaching implications for the computational simulation and optimization of semiconductor devices.

I. INTRODUCTION

Semiconductor technologies have shaped our digital societies and are becoming instrumental to the generation of renewable energy by photovoltaic and photocatalytic means. The performance of these devices depends not only on the electronic properties of their semiconducting constituents but also on the electrical characteristics of their contact regions — i.e., the junction between two semiconductors or the interface of a semiconductor with a metallic lead or ionic solution.

The electrical quality of these contact regions is determined by the Schottky barriers which develop at the semiconductor surface. Schottky barriers arise due to the difference between the energy of an electron in the semiconductor and the corresponding energy in the contacting material. The height of the Schottky barrier \( \phi_s \) sets an upper limit to the density of the current \( j \) that tunnels across the junction under an applied bias \( \eta \) by controlling the activation of the current–voltage response

\[
j = j_0 \exp \left( -\frac{e \phi_s}{k_B T} \right) \left[ \exp \left( \frac{e \eta}{k_B T} \right) - 1 \right],
\]

Here, \( j_0 \) denotes the kinetic prefactor of the current density, \( e \) is the charge of an electron, \( k_B \) stands for the Boltzmann constant, and \( T \) is the ambient temperature.

Small variations in the Schottky barrier heights translate into large differences in the intensity of the current. In quantitative terms, varying the Schottky barrier height from 0.2 to 0.4 V causes the current to decrease by a factor of \( \sim 10^3 \). In view of the strong influence of the Schottky barriers on the performance of optoelectronic and photocatalytic junctions, there is a need across the field of computational solid state physics to predict their magnitude as a function of the structure of the interface.

In this work, we predict Schottky barriers from first principles using a long-range description of the bending of the electronic bands. Critical to this model is the ability to capture the influence of the surface states, induced by the chemical termination of the interface, on the decay of the electric field within the semiconductor. The newly proposed model provides the ability to evaluate Schottky barriers under realistic conditions, beyond a short-range representation of the neutral junction.

II. THEORETICAL BACKGROUND

To describe this model, we first examine the formation of Schottky barriers at the interface between an intrinsic semiconductor and a chemically inert medium. We consider the simplest case of a semiconducting electrode
in contact with an ideal electrolyte, which does not interac-
tively the applied voltage, the equilibrium of the system will take place without constraint on the Fermi energy of the electrode; as a result, no electronic charge will be injected or withdrawn from the semiconductor. Figure 1a depicts the resulting equilibrium state, where a surface dipole forms due to the charge that spills out from the electrode and to the solvent molecules that re-
orient in the proximity of its surface. The dipole can be expressed as \((\delta \chi_s^m) = (\Delta_s) - (\Delta_m)\), where \((\Delta_s)\) and \((\Delta_m)\) are the differences between the Fermi levels and average electrostatic potentials for the semiconductor and the medium\(^7\).

Once defects are introduced to the semiconductor and chemically active ionic species are added to the embedding electrolyte, the chemical stability window of the electrolyte will be reduced, causing the Fermi level of the electrode to be pinned by the chemical potential of the reaction that limits the stability of the reactive medium. This constraint leads to a different equilibrium state (Fig. 1b), where defect charge builds up within the depletion layer of the electrode and compensating ions accumulate within the double layer of the electrolyte. As a result, a large drop in the electrostatic potential is observed, corresponding to an increased surface dipole \(\delta \chi_s^m\), a potential drop within the depletion layer of the electrode that corresponds to the Schottky barrier \(\varphi_s\), and another electrostatic shift in the electrical double layer \(\varphi_m\)\(^8,9\).

In this new equilibrated state, the Schottky barrier \(\varphi_s\) is related to the surface dipole through

\[
\varphi_s = \Delta_s - \Delta_m - \delta \chi_s^m - \varphi_m, \tag{2}
\]

where \(\Delta_s\) and \(\Delta_m\) are the differences between the Fermi level (divided by the electron charge \(e_0\)) and the bulk potential of the doped semiconductor and the chemically active medium, respectively. An electrostatic shift \(\varphi_m\) will also take place in the medium. Since the carrier concentration of a metal or solution is typically orders of magnitude greater than that of the semiconductor, the potential drop within the medium will be negligible, i.e., \(\varphi_m \ll \varphi_s\). (The potential drop within the medium can even be eliminated by varying the potential and pH of the solution to find the zeta potential, the point at which there is net zero interface charge due to the interfacial accumulation of \(H^+\) and \(OH^-\) species\(^10,11\).)

Predicting the Schottky barrier of a semiconductor interface from first principles is challenging; since a barrier height of 0.5 V across a semiconductor with a dielectric constant of \(\sim 10\) and a carrier density of \(10^{16} \text{ cm}^{-3}\) would extend as far as \(\sim 250 \text{ nm}\) into the semiconductor, the direct quantum-mechanical modeling of Schottky barriers is prohibitively demanding using current computational resources. Most previous first-principles density-functional theory studies instead attempt to compute Schottky barriers by focusing solely on electrically neutral surfaces with a simulation distance on the order of \(\sim 10\) nm. The interfacial dipole between an intrinsic semiconductor surface and a pure embedding medium \((\delta \chi_s^m)\) is found and any remaining difference between the Fermi levels is attributed to the Schottky barrier\(^12-19\). This approach overestimates the barrier height, as can be seen by rearranging Eq. 2:

\[
\varphi_s = (\Delta_s - (\Delta_m) - (\delta \chi_s^m) - (\delta \chi_m^m))^{-} - (\delta \chi_s^m - (\delta \chi_m^m)^{-}). \tag{3}
\]

where use has been made of the fact that \(\varphi_m \ll \varphi_s\). In many cases, calculating only the first half of the right hand side of Eq. 3, as these methods do, turns out to be a reasonable approximation; the overestimation of the Schottky barrier height may fortuitously be compensated by the underestimation of the band gap within local and semilocal density-functional theory. Nevertheless, this approach is applicable only for moderately charged interfaces (i.e., \(\delta \chi_s^m \approx (\delta \chi_m^m)^{-}\)), and a framework that correctly calculates the surface dipole, incorporating the effects of surface termination and external bias, is generally preferable.

We address the length-scale limitation mentioned above by employing a first-principles approach that integrates an implicit semiclassical description of the bulk semiconductor with an explicit electronic-structure treatment of the semiconductor surface. This method allows us to directly determine the potential-dependent interfacial dipole and the resulting equilibrium Schottky barrier heights. We demonstrate the significant impact adsorbates can have on these results, finding the charge–voltage curves and electrochemical stability of different surface terminations of the silicon–water system. Finally, we show how charge trapped at surface states reduces the Schottky barrier and the current density of semiconductor electrodes.

The first step of this analysis is to embed explicit quantum-mechanical calculations of the semiconductor surface layers into an implicit continuum model of the bulk semiconductor and bulk water. Following the approach of Ref. 20, we create a five layer thick slab of semiconductor material, representing the surface of the electrode, which we model quantum-mechanically. This allows us to explicitly calculate the surface dipole \(\delta \chi_s^m\). To connect this slab to its surroundings, we place it in equilibrium with a Poisson–Boltzmann statistical distribution of ions on the solution side and a Mott–Schottky profile of electrostatically activated defects on the semiconductor side. By aligning the asymptotic electrostatic reference in the bulk water region, we can relate the calculated Fermi levels to the hydrogen reference electrode. For our calculations, we use Quantum-Espresso with a self-consistent continuum solvation (SCCS) model\(^21,22\), along with the Perdew–Burke–Ernzerhof exchange correlation with the projector augmented wave (PAW) representation of the ionic cores\(^23,24\). (See Sec. S2 of the supporting information for a detailed description of the computational model.)
III. RESULTS AND DISCUSSION

To systematically examine the effects of surface electrification, we simulated seven representative silicon 1×1 (110) surfaces terminated by different combinations of oxygen and hydrogen species: O, (O,H), 2O, (2O,H), (4O,H), H, and 2H as shown in Fig. 2a. We used a dopant concentration of $10^{18}$ cm$^{-3}$. The calculated charge–voltage responses for the different surface terminations are shown in Fig. 2b. The potentials are measured with respect to the flatband potential $\varphi_{FB}$, i.e., the potential of an electrically neutral semiconductor junction that induces no band bending. From the charge–voltage plots alone, it is clear that substantial differences in the electrical response can be introduced by altering the surface termination of a photoelectrode. This trend indicates that these terminations induce a significant surface dipole $\delta \chi_m$, arising from charge trapping at the electrode surface. However, surface terminations with low charge accumulation (e.g., 2H), induce an extended distribution of charge throughout the bulk semiconductor. This observation is consistent with the fact that the charge within the semiconductor creates a potential drop orders of magnitude larger than the surface dipole induced by the same charge caught at the surface, due to poor electrostatic screening in the space-charge region. In contrast, surface terminations with significant charge accumulation as a function of applied bias (e.g., the O and 2O covered surfaces), have most of their charge trapped within the surface dipole.

Figure 3 confirms this observation by showing the redistribution of the surface charge under applied voltage; for most of the surfaces, charge accumulates almost entirely at the surface adsorbate. For the 2H-terminated surface, however, charge is distributed through all five layers of the simulated semiconductor, indicating that the charge extends deep into its depletion layer.

With the charge–voltage relationships in hand, we can then calculate the surface free energy of each surface termination as a function of potential using the Lippmann electrocapillary equation

$$\gamma = \gamma_0 - \int_{\varphi_{FB}}^{\varphi} \sigma(\Phi) d\Phi.$$}

Here, $\sigma$ is the charge per surface area of the electrode, $\gamma$ is the surface free energy of the charged slab at a certain potential $\varphi$, and $\gamma_0$ is the surface free energy of the slab under neutral charge conditions at the flatband potential. We determine the surface free energy of a charge neutral surface by subtracting the energy of a surface
FIG. 4. The equilibrium barrier height as a function of the difference between the hydrogen evolution potential and the flatband potential. An ideal semiconductor junction, would show a unit slope, \( \mathcal{S} = 1 \) (dashed line). Due to charge trapping by surface states, the Schottky barrier heights are significantly reduced, corresponding to a charge-pinning fraction equal to \( \mathcal{S} = 0.7001 \) for the silicon–water system.

terminated with adsorbates from the energy of the same surface without adsorbates and further subtracting the energy required to pull out a given adsorbate from the surrounding solution (see Sec. S4 of the supporting information). We then calculate the free energy curves for each surface, as shown in Fig. 2c. The structure with the lowest free energy at a given electrode potential is the most stable. Under most potential and pH conditions within the stability window of water, the (4O,H) configuration (i.e., the most oxidized termination tested) is the most stable, in agreement with the known tendency of silicon to oxidize in contact with water\(^{25,26}\).

Next, we turn our attention to the relationship between the surface termination of an electrode and the fraction of the total potential drop accommodated by the space charge region of the material in an effort to estimate the Schottky barrier. To this end, we introduce the space charge fraction, \( \theta_s = \varphi_u / (\Delta_s - \Delta_m) \), to quantify the extent to which surface states dominate the electrical response of the photoelectrode. As shown in Fig. 2d, at low applied bias, the majority of the potential drop across the electrode can be found in the surface dipole \( \delta \chi^m \), leading to a low space-charge fraction. The potential drop taking place across the semiconductor increases rapidly with applied bias, then levels off after 0.3-0.4 V. These asymptotic values can be seen as a measure of the amount of charge distributed throughout the space-charge region of the semiconductor when an external bias is applied. The surface termination with the least surface charge trapping, 2H, exhibits the highest \( \theta_s \) asymptote.

Having computed the Schottky barrier as a function of external bias, we can now calculate an important empirical parameter, the charge-pinning fraction \( \mathcal{S} \), which describes the reduction of the Schottky barrier from its theoretical maximum due to charge trapping\(^{27-32}\). Explicitly, the charge-pinning fraction is defined as:

\[
\varphi_u = \mathcal{S} (\chi_m - \chi_s),
\]

where \( \mathcal{S} = 1 \) corresponds to an ideal semiconductor junction with no charge trapping, while a value of \( \mathcal{S} = 0 \) indicates all the charge is caught in surface states, inducing complete Fermi-level pinning. Here, \( \chi_m \) and \( \chi_s \) are the vacuum referenced electronegativities of the embedding medium and the semiconductor, respectively. The value of \( \mathcal{S} \) is typically obtained experimentally by measuring the Schottky barrier of a semiconductor against different chemical environments and then fitting the barrier–electronegativity relationship.

To calculate the equilibrium Schottky barrier \( \varphi_u \) and charge-pinning factor \( \mathcal{S} \) of each silicon termination, we set the potential of the electrodes to the hydrogen evolution potential. We then directly extract the Schottky barrier height by calculating the potential drop within the bulk semiconductor. By plotting the Schottky barrier height as a function of the applied bias at the potential of the hydrogen evolution reaction, as shown in Fig. 4, we can find the charge-pinning fraction from the slope. Using a linear regression, we measure a slope of \( \mathcal{S} \approx 0.7 \), which corresponds to a significant deviation from the ideal trend of \( \mathcal{S} = 1 \), reflecting the contribution from the surface dipole to the renormalization of the Schottky barrier height.

Our work highlights contradictory requirements that limit the photocatalytic activity of semiconductor electrodes. For the hydrogen evolution reaction, the ideal Schottky barrier would be positive — driving electrons from the bulk of the electrode to the surface. The two terminations with the most positive Schottky barriers (one oxygen and two oxygens adsorbed onto the surface), however, are both unstable in the stability window of water as shown in Fig. 2c. The difficulty of simultaneously achieving surface stability and effective charge transfer across the silicon–water interface provides quantitative molecular-level insights into the limited photocatalytic activity of silicon photoelectrodes in an aqueous environment.

IV. CONCLUSION

In summary, we have developed a complete model of the bending of electronic bands at a semiconductor surface to calculate the height of the electronic barriers. This model enables us to extract and confirm the empirical linear dependence of the Schottky barrier as a function of the relative position of the donor and acceptor levels, showing the critical influence of charge trapping in reducing the current density of the junction. The model provides a first-principles interpretation to empirical relations of pivotal importance to the experimental
study of electrified junctions. In conjunction with recent developments in the electronic-structure prediction of semiconductor band gaps, our work opens up the possibility of assessing the electronic factors that control the current–voltage response and optoelectronic behavior of semiconductor junctions from first principles.

**ACKNOWLEDGMENTS**

The authors acknowledge primary support from the National Science Foundation under Grant DMR-1654625, and partial support from the 3M Graduate Fellowship and Penn State University Graduate Fellowship. The authors gratefully acknowledge Giulia Galli, Héctor D. Abruña, Roman Engel-Herbert, and Suzanne Mohney for fruitful discussions.

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Supporting Information: “Prediction of Schottky Barriers at Electrified Junctions”

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FIG. S1. Three possible conventions in describing a semiconductor junction. (a) Alignment of the semiconductor and medium by the average bulk Hartree potential. The difference between the Fermi levels in this alignment can be characterized as $\Delta_s - \Delta_m$ where $\Delta_s$ and $\Delta_m$ are the difference between the Fermi level and the bulk Hartree potential of the materials. (b) Alignment by the vacuum level. Here, the primary values are the electronegativities of each material, $\chi_s$ and $\chi_m$. Importantly, the difference between Fermi levels in this alignment does not include the electrostatic potential difference between the bulk Hartree potential and vacuum of the semiconductor and embedding medium, $\delta \chi^v_s$ and $\delta \chi^v_m$ respectively. (c) Alignment by Fermi levels, as would take place in equilibrium. The difference between the two bulk Hartree potentials can now be quantified as the surface dipole $\delta \chi^p_s$ in addition to the Schottky barrier $\varphi_s$. Calculations of the Schottky barrier need to be careful in understanding which alignment they are referring to when making measurements.

1. ALIGNMENT OF SEMICONDUCTOR AND MEDIUM POTENTIALS

Figure S1 shows three different conventions for aligning potentials between the semiconductor and the embedding medium. While in the context of first-principles calculations, potentials have traditionally been aligned potentials based upon the bulk Hartree potential as shown Fig. S1a, the electrochemical community has typically defined potentials based on the electronegativities $\chi_s$ and $\chi_m$ as shown in panel b. In reality, of course, it is the Fermi level that is brought into equilibrium as shown in panel c. All of these methods can be used to find the Schottky barrier as long as one is careful with alignment, specifically noting that the difference between electronegativities does not take into account the voltage difference between the bulk average Hartree potentials of the semiconductor and embedding medium, i.e., $\delta \chi^v_s - \delta \chi^v_m$.

2. COMPUTATIONAL DETAILS

These results build upon implicit solvation models, which create dielectric cavities around each lateral facet of the DFT slab with local dielectric permittivities written on the semiconductor side as

$$\epsilon(r) = \exp[(\zeta(r) - \sin(2\pi\zeta(r))/2\pi) \ln \epsilon_{sc}]$$  

(1)

where $\epsilon_{sc}$ is the dielectric constant of the bulk of the semiconductor and $\zeta(r) = (\ln \rho_{max} - \ln \rho(r))/(\ln \rho_{max} - \ln \rho_{min})$ is used as a smooth switching function, marking the transition between the quantum and continuum regions. Here, $\rho_{min}$ and $\rho_{max}$ serve as the density thresholds specifying the inner and outer isocontours of the dielectric cavity. The same equations can be used on the solution side with $\epsilon_{sc}$ replaced by $\epsilon_{sol}$, the dielectric constant within the solution. We then find a cutoff value a few layers within the slab at the inflection point of the potential and apply a semiconductor charge potential relationship to find the potential of the bulk semiconductor, found with

$$\bar{\Phi}_0 = \bar{\Phi}(z_c) - k_B T - \frac{\epsilon_0}{2N} \left( \frac{d\Phi}{dz} (z_c) \right)^2$$  

(2)

for an n-type semiconductor. Here, $\bar{\Phi}_0$ is the bulk potential of the semiconductor, $\bar{\Phi}(z_c)$ is the macroscopic potential difference between a charged slab and a neutral slab at the cutoff $z_c$, and $N$ is the dopant concentration of the semiconductor electrode. To find the Fermi level within the bulk of the semiconductor, we calculated the Fermi level of a slab with no charge on it and added it to the bulk potential found earlier.
We used Quantum-Espresso for our DFT calculations\textsuperscript{3}. Five layer slabs were determined to be sufficient for convergence of the Fermi level, with the left three layers frozen to represent a bulk semiconductor. We centered the slab in the supercell with a vacuum height of 7 Å. We used pseudopotentials generated with Perdew–Burke–Ernzerhof exchange correlation with the projector augmented wave (PAW) method from the SSPP library\textsuperscript{2–4} with kinetic and charge density cutoffs of 50 Ry and 750 Ry, respectively. The Brillouin zone was sampled with a shifted $5 \times 5 \times 1$ Monkhorst–Pack grid and 0.03 Ry of Marzari–Vanderbilt smearing\textsuperscript{5}. We used the ENVIRON module for the calculation of continuum dielectric solvent regions with the parametrizations developed for water\textsuperscript{6}. This allowed us to create a dielectric cavity of water on one side of the slabs with a dielectric constant of 78.3, and a dielectric cavity with a dielectric constant of 11.7 representing the bulk silicon semiconductor on the other side. We used a dopant concentration of $10^{18}$ cm$^{-3}$ to calculate the semiconductor interfacial potential drop.

3. ANALYTICAL MODEL OF CHARGE–VOLTAGE DATA AND CHARGE-PINNING FRACTION

To describe the electrical response of semiconductor–solution interfaces more precisely, we developed an analytic model to describe the charge–voltage curve of a photoelectrode. This model is based on the observation that surface states in the system induce a metal-like constant capacitance, an assumption verified by looking at the slab’s density of states. These surface states are then connected to an ideal semiconductor. Looking at the charge–voltage curves for just surface states and just the bulk semiconductor, it becomes clear that both the voltages and the charges across the bulk semiconductor and surface state elements add together, making it necessary to develop a system that combines both these aspects of having two capacitors in series or parallel. This system is described as follows:

$$Q = \sqrt{2\epsilon_0 \epsilon_s \epsilon_0 N \sqrt{\gamma_{sc}(\varphi)}} + \mathcal{C}_{ss}(1 - \gamma_{sc}(\varphi)) \varphi$$

(3)

where $\mathcal{C}_{ss}$ is the capacitance of the surface states, a constant that is obtained from fitting, $\epsilon_s$ is the dielectric constant of the semiconductor, $\Phi$ is the potential drop across the semiconductor–electrolyte interface, $\mathcal{N}$ is the dopant concentration of the semiconductor, and $\gamma_{sc}$ is the fraction of potential on the electrode that falls within the bulk of the semiconductor, i.e. the space-charge fraction. This fraction is not a constant and changes as a function of the total potential across the electrode.

An expression for $\mathcal{S}$ can be derived by noting that the amount of charge on the semiconductor region of the electrode is almost always roughly a constant fraction of the charge on the surface states for the materials we sampled, as demonstrated in Figure S2. This can be formalized as

$$q_{sc} = \eta q_{ss}$$

(4)

where $\eta$ is the fraction of the charge on the surface states that resides within the semiconductor section, and $q_{sc}$ and $q_{ss}$ are the charge on the bulk of the semiconductor and the charge in the surface states respectively. This allows us to get an expression for $\gamma_{sc}$ as follows:

$$\gamma_{sc}(\varphi) = 1 + \frac{\varphi_{sw}}{\varphi} - \sqrt{\left(\frac{\varphi_{sw}}{\varphi}\right)^2 + \frac{2\varphi_{sw}}{\varphi}}$$

(5)

where

$$\varphi_{sw} = \frac{\epsilon_0 \epsilon_s \epsilon_0 \mathcal{N}}{\eta^2 \mathcal{C}_{ss}}$$

(6)

is in units of Volts and can be considered the switching potential, representing the potential at which 26% of the total potential drop takes place across the bulk semiconductor. At potentials above the switching potential, the fraction shifts rapidly such that the bulk semiconductor potential drop will make up the majority of the total potential drop across the electrode. The charge–voltage model for the semiconductor–solution interface can now be fully described analytically by finding the two constants $\eta$ and $\mathcal{C}_{ss}$. The surface state capacitance, $\mathcal{C}_{ss}$, can be found by examining the charge-voltage results for solely the surface states. From here, $\eta$ can be fitted to the overall charge–voltage curve, which will also match observations of $\eta$ from the first principles calculations. The values found for $\eta$ and $\mathcal{C}_{ss}$ are shown in Table I.
FIG. S2. The constancy of $\eta = q_{sc}/q_{ss}$ as a function of potential.

TABLE I. Fitted surface state properties for the seven surface configurations tested. The fraction of the charge on the surface states that is on the bulk of the semiconductor is represented by $\eta$. The capacitance of the surface state, assuming a metal like distribution, is represented as $C_{ss}$. The effective dopant concentration of the material from measuring the slope of a Mott–Schottky graph without adjusting for surface states is represented as $N_{eff}$.

| $\eta$ | $C_{ss}$ ($\mu$F cm$^{-2}$) |
|--------|-----------------------------|
| O      | 0.044                       | 17.3 |
| (O,H)  | 0.060                       | 14.0 |
| 2O     | 0.040                       | 17.6 |
| (2O,H) | 0.063                       | 13.1 |
| (4O,H) | 0.067                       | 8.1  |
| H      | 0.087                       | 14.8 |
| 2H     | 0.173                       | 10.5 |

4. DERIVATION OF SURFACE ENERGY

The free surface energy of a surface with $N_H$ hydrogen adsorbates, $N_O$ oxygen adsorbates, and $q$ surface free charges can be found as follows:

$$G(N_H, N_O, q) = G(N_H, N_O, 0) + \int_0^q \varphi(q')dq',$$

where $\Phi$ represents the electrical potential of the interface with $q'$ free charges on it. To find $G(N_H, N_O, 0)$ we take the DFT energy of this structure, $E(N_H, N_O, 0)$, and subtract the DFT energy of a silicon surface with no adsorbates, $E(0, 0, 0)$. We additionally subtract the energy of taking a hydrogen ion $\mu(H^+)$ or hydroxyl ion $E(OH^-)$ out of solution:

$$G(N_H, N_O, 0) = E(N_H, N_O, 0) - E(0, 0, 0) - (N_H - N_O)\mu(H^+) - N_O\mu(OH^-).$$

The energy of hydrogen ions in solution can be found from the following reaction

$$H_{aq}^+ + e^- \leftrightarrow 1/2H_2(g)$$

which is at equilibrium at the potential of the reversible hydrogen electrode. Therefore the energy of $H^+$ is

$$\mu(H^+) = 1/2E(H_2) - \varphi(SHE) - 0.06pH.$$
FIG. S3. The calculated Pourbaix diagram for the Si (110) surface in contact with water, accounting for the energy from charge trapping at the semiconductor–solution interface. This diagram shows what adsorbate structure will be most stable at different values of the electrode potential and solution pH. At low pH, Si will be most stable with two hydrogen adsorbed, but at the majority of normal conditions, the most oxidized form of silicon tested will be the most stable, matching experimental observations of the rapid oxidation of silicon in water.

where $E(H_2)$ is the DFT energy of hydrogen gas.

Similarly the energy of $O^{2-}$ can be found by first finding the energy of $OH^-$ taken out of solution. The energy of $OH^-$ can be found from the reactions

$$1/2O_2(g) + 2H^+ + 2e^- \leftrightarrow H_2O$$  \hspace{1cm} (11)

and

$$1/2O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$$  \hspace{1cm} (12)

which are at equilibrium at the water splitting potential 1.23 V (RHE).

Combining these equations and plugging in the previously calculated formula for $H^+$ gives

$$\mu(OH^-) = 1/2E(H_2) + 1/2E(O_2) + \varphi(SHE) - 2*1.23V + 0.06pH.$$  \hspace{1cm} (13)

where $E(O_2)$ is the DFT energy of an oxygen molecule.

With these equations in hand, the free energy at the surface can now be easily calculated as a function of pH and voltage. We went on to calculate a pourbaix diagram of the most stable phase at several solution pH values and voltages as shown in Figure S3. It is important to note that we only found the lowest energy of the seven different adsorbate configurations tested, assuming the number of adsorbates stays the same and configurational entropy is not included. This model could be extended to take into account the full change in adsorbate coverage with potential with a Monte Carlo or cluster expansion model.

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