



Hot Electron Chemistry at Solid-Liquid Interfaces

**Robert Hamers
UNIVERSITY OF WISCONSIN SYSTEM**

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Hot Electron Chemistry at Solid-Liquid Interfaces

Robert J. Hamers, Gilbert M. Nathanson, Jordan R. Schmidt

Department of Chemistry, University of Wisconsin-Madison

FA9550-14-1-0220

Abstract

The facile generation of solvated electrons and hydrogen atoms in water can enable local and sustainable industrial processes such as the production of ammonia and destruction of toxic waste. We have investigated the use of easily fabricated solid-state devices to generate these species electrochemically in water. We fabricated highly doped silicon wafers coated with thin films of insulating SiO_2 and high k dielectric HfO_2 , either bare or covered with gold. These devices rely on quantum mechanical tunneling of electrons from silicon through the insulating oxide layer directly into water. These electrons rapidly thermalize and become solvated. In addition, hydrogen atoms may be generated in the SiO_2 layer, which then diffuse into solution. In both cases, reactive species are injected into the solvent itself and delivered to the companion reactant, bypassing reactions at the electrode surface. The chief competing reaction is hydrogen evolution, which must be minimized to achieve high selectivity. Our attempts to synthesize ammonia from water and dissolved nitrogen gas were unsuccessful because of overwhelming H_2 production, but the successful decomposition of chloroethanol to ethanol radical and chloride anion in water demonstrates a new and powerful way to destroy toxic waste.

Introduction and Motivation

Accessing energetic electrochemical reactions is typically limited by the electrochemical stability range of the solvent. In aqueous media, this limits the ability to form energetic chemicals species such as hydroxyl radicals, atomic hydrogen, and solvated electrons. The basis for this project is the observation that excitation of diamond with above-bandgap light produced photoemission of electrons into water.¹⁻⁴ The resulting solvated electrons were detected directly by transient absorption spectroscopy,² and fundamental and important processes such as reduction of N_2 to NH_3 ⁴ and reduction of CO_2 to CO were characterized.³ In the present project, we aimed to explore whether reactive chemical species in water can be produced *electrochemically* rather than photochemically. This goal presents enormous challenges because of competition from hydrogen evolution. As described below, we attempt to suppress H_2 production by building metal-insulator structures that are designed to exploit thin tunneling barriers as a means to create high-energy reactive species. These devices use only modest applied voltages and currents, below those conventionally associated with plasma formation.

An attractive low-voltage method to generate aqueous electrons relies on building a sandwich structure in two configurations: 1) a thin insulator placed on top of a metal, and 2) the same thin insulator placed between two planar conductors. A voltage is applied across the insulator until a triangular barrier is achieved, resulting in electrons tunneling through the insulator. Figure 1 depicts the three-element structure that we refer to as a “water transistor” due to its close analogy to a bipolar

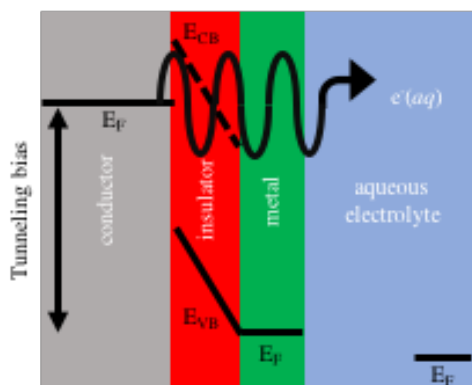


Figure 1: Electron tunneling across a thin insulator

transistor: Electrons emitted from a substrate (the emitter) pass through a thin conductive region (the base) and pass into the aqueous medium (the collector). Previous studies showed that aluminum metal coated with very thin (2.5 nm) layers of Al_2O_3 and then coated with 15 nm Ag film were able to directly inject electrons into an adjacent aqueous electrolytic solution⁵⁻⁶ and

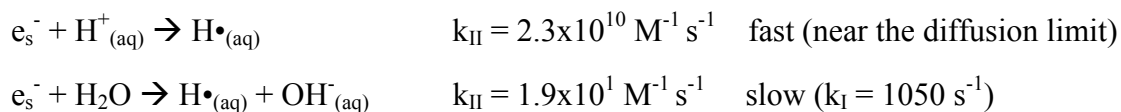
produce solvated electrons in aqueous solution using $< 10\text{V}$.⁷ However, these previous studies relied primarily on formation of electroluminescent probes as a detection technique and did not extend to electrochemical conditions significantly outside the solvent window of water, such as N_2 or CO_2 reduction.

In our work, we investigate both 3-electrode and 2-electrode geometries. A 2-electrode geometry, in which the middle conductor layer is eliminated, can also be effective, albeit providing somewhat less independent control of the band positions. The first section below focuses on both metal-insulator and metal-insulator-metal structures in the form of a highly doped silicon ($\text{n}^+\text{-Si}$)/silicon oxide (SiO_2) two element device and an $\text{n}^+\text{-Si/SiO}_2/\text{Au}$ three-element device. We first attempted to use these devices to synthesize ammonia from just water and dissolved nitrogen gas. Despite intensive studies, we were unable to demonstrate substantial NH_3 production, mostly likely because of intense competition from H_2 production both at the electrode surface and in solution. We then replaced the insulator SiO_2 with an even higher dielectric constant insulator, hafnium oxide (HfO_2), a substitution that enhances electron tunneling. We also moved our focus on ammonia synthesis using dissolved N_2 in water to dehalogenation of dissolved chloroethanol in water, allowing us to increase the concentration of the reactant by orders of magnitude. These changes indeed allow us to observe a true electron-induced reduction of a solute in water facilitated by a solid-state electron emitter at low voltage. These two projects are described in detail below.

I. Electrochemical Ammonia Synthesis by Earth (silicon), Air (nitrogen), Fire (electricity), and Water via the Solid-State Generation of Hydrated Electrons and Hydrogen Atoms

The efforts described in this section by graduate student Wen-Tsung Huang are directed at creating and harnessing reactive species in solution using simply fabricated solid-state devices at low voltage. Our central tests are the production of ammonia from just water and dissolved nitrogen, along with current-voltage characteristics of the devices. Midway through the grant period, we realized that solvated electron production via the application of an applied voltage to diamond was extremely challenging. We were unable to produce ammonia from diamond, even using an interdigitated pattern with small gaps and high electric fields to promote emission of electrons into water. We then turned our attention to several reports in the literature that demonstrated production of solvated electrons and hydrogen atoms in water by metal-insulator and metal-insulator-metal devices.⁷⁻¹⁴ By using these devices, we again seek to generate ammonia from nitrogen dissolved in water.¹⁵ This synthesis, particularly with electrodes that do not contain precious metals, would provide a truly sustainable model for small-scale production of ammonia when the electrons are provided by solar cells exposed to sunlight.

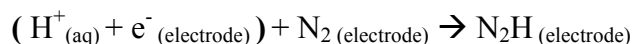
Solvated Electron and Hydrogen Atom Reactions. The generation of ammonia from N₂ and water begins with the formation of hydrogen atoms from solvated electrons e_s⁻:¹⁶



Together, these reactions limit the lifetime of e_s⁻ to about 0.2 ms in pure water at pH = 7 before H atoms are produced. In the presence of dissolved N₂, our aim is to use solvated H atoms to attack the extremely strongly bound N atoms in N₂ in a slow, rate-limiting step:

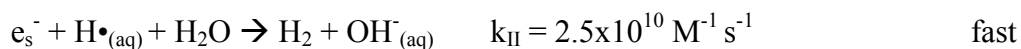


The N₂H intermediate may also be produced by attack on N₂ adsorbed at the electrode surface:

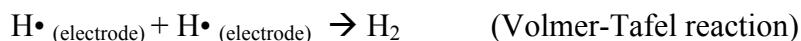


The addition of H to N₂ is the key step in ammonia synthesis and is in constant competition with hydrogen evolution via five different reactions in solution and at the electrode surface:

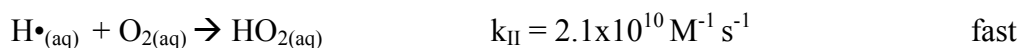
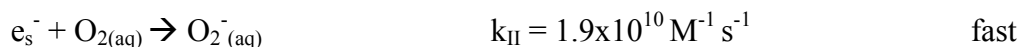
Reactions in solution:



Reactions at the electrode surface:¹⁷



In addition, dissolved O₂ is present whenever N₂ is derived from air and whenever the anode reaction producing O₂ is connected to the cathode compartment. In this case, O₂ acts as both an electron and hydrogen atom scavenger in solution:¹⁶



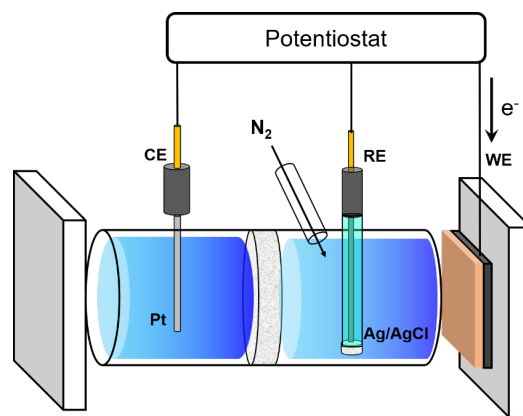
The extreme competition from these rapid reactions highlights just how challenging ammonia synthesis can be for electrodes immersed in aerated water.

Solid-State Production of Solvated Electrons and Hydrogen Atoms. We have tried to carefully design and fabricate devices and electrochemical cells that minimize hydrogen evolution and oxygen-electron reactions. The need to selectively suppress H₂ production has long been recognized, and early researchers realized that H₂ could be minimized by choosing electrodes that expose oxide films rather than metals to water in order to avoid facile metal-catalyzed H₂ formation. The transport of electrons to the oxide surface and into solution is achieved by quantum mechanical tunneling of electrons through the oxide layer. If the layer is thin enough, electrons will ballistically tunnel through the oxide and be directly injected into the conduction band of water.⁷⁻⁹ However, such oxide films were found to rapidly decay when exposed to water and continuous applied voltages.¹⁸ To circumvent this destruction, pulsed voltages may be used. Alternatively, the oxide layer can be coated with a thin layer of metal, with the intent that the ballistic electrons will continue through the metal film and still enter the conduction band of water. These high-energy (“hot”) electrons will then undergo collisions with water molecules and thermalize within one picosecond, proceeding to a fully equilibrated and solvated state e_s⁻ within an additional picosecond. This solvated (or hydrated) electron is enormously reactive and perhaps the most powerful reducing agent in water, with a reduction potential of -2.87 volts versus the standard

hydrogen electrode.

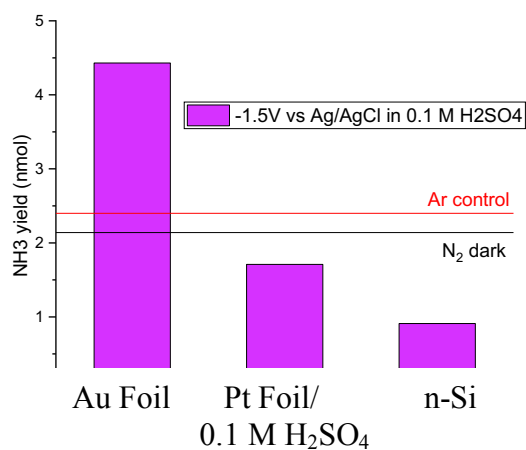
The Search for Solid-State

Electrochemical Ammonia Production. We describe three efforts to construct inexpensive solid-state devices and synthesize ammonia from just nitrogen and water. The electrochemical cell is shown in the figure on the right. It contains



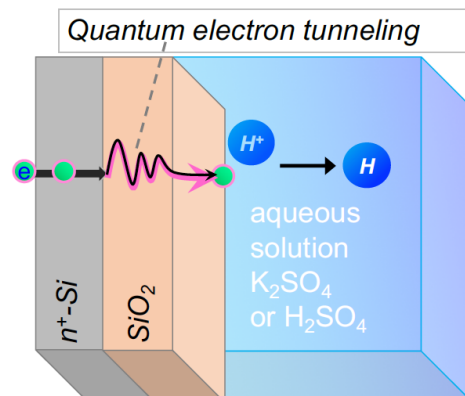
an anode (Pt counter electrode CE) and cathode (working electrode WE) compartments separated by a glass frit. N₂ gas enters the cathode region, which also includes an Ag/AgCl reference electrode RE. The electrolytes were chosen to contain inert anions: 0.1 M K₂SO₄ and 0.1 M H₂SO₄ (to supply H⁺ ions). This device may also be used to record the current and voltage characteristics of each working electrode. The indophenol blue method is used to detect ammonia at the nanomole scale. We expended great effort to carefully calibrate the ammonia measurements and to clean the cell in order to remove ubiquitous ammonia contaminants. In particular, we perform two reference measurements for comparison: 1) the substitution of argon for ammonia and 2) experiments with N₂ but with no applied voltage (“dark”). These calibration measurements indicate that we are sensitive to ammonia production that exceeds approximately 2 nanomoles of NH₃ over a two-hour interval.

We first remark that more traditional electrodes such as platinum, gold, and highly negatively doped (nearly metallic) silicon have all been tested. This silicon sample, heavily doped with arsenic as an electron donor, is labeled as n⁺-Si. Gold foil does indeed make ammonia from N₂ and H₂O, as shown in the figure below. In this graph, the y-axis is the amount of NH₃ produced in nanomoles and the x-axis refers to the different experiments. The solid lines refer to the Ar and N₂/no voltage reference experiments. In all of the experiments reported here, only ammonia produced by the gold foil significantly exceeds the reference experiments. Its drawback is an enormous production of H₂ gas as well, which is so large that H₂ bubbles out



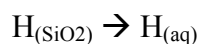
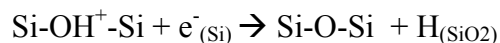
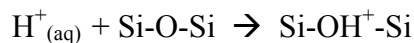
of solution.

n⁺-Si/SiO₂ Electrode. As described above and shown in the figure on the right, we use this metal-insulator device to create ballistic electrons by quantum mechanical tunneling through the thin (5 and 11 nm) silicon oxide layers. We found, as did others, that continuous potentials more negative than -2 V leads to destruction of the SiO₂ oxide overlayer.¹⁸ An applied potential of at least -2.8 volts is required to produce solvated electrons, based on the energy diagram of the n⁺-Si/SiO₂/H₂O system.

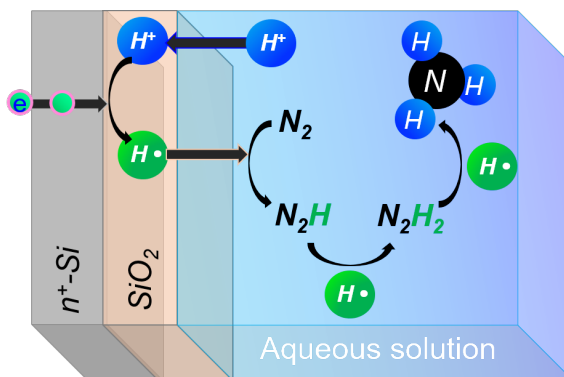


As an alternative, we substituted short pulses for a continuous applied potential, which slows the oxide decay. Even with -7 V pulses (100 Hz, 1 ms duration) and instantaneous currents of 10 mA, however, we were unable to detect ammonia above the background. This result suggests that most solvated electrons produced by n⁺-Si/SiO₂ react to form H₂ gas, although we did not detect H₂ directly. The ammonia measurements are shown in the histogram at the end of the document, which includes all of our measurements over two-hour intervals.

At about this time, we read a literature report of an entirely new route to making H atoms with this n⁺-Si/SiO₂/H₂O device. At voltages of less than -2 V, the following reaction can occur, as illustrated in the figure on the right:¹⁴

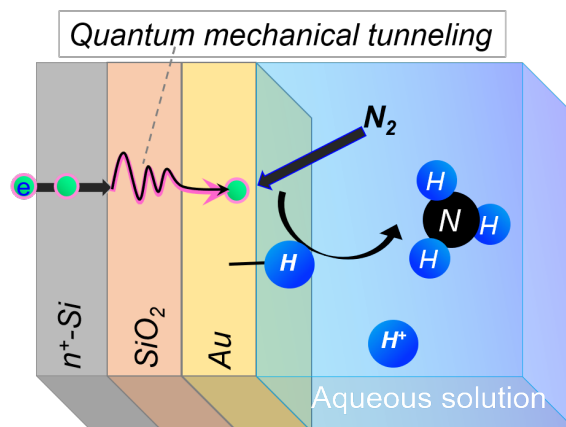


The hydrogen atoms produced in the thin SiO₂ layer



can then diffuse back into solution, creating a ready source of solvated H atoms that bypass solvated electron production. These H atoms may then attack dissolved N_2 and ultimately produce NH_3 , as depicted in the figure above. We intensively investigated this scenario, and reproduced the current-voltage characteristics from the literature. Unfortunately, we were unable to produce ammonia at levels beyond the control experiments at applied voltages of -1.5 and -2.0 V that are known in the literature to produce H atoms. These negative results are shown in the histogram at the end, most likely reflecting the facile combination of solvated H atoms into H_2 . We reluctantly set aside this device and pursued a more complex metal-oxide-metal sandwich.

n^+ -Si/SiO₂/Au Electrode. As shown in the figure below, the SiO₂ oxide layer is covered with a thin 20 nm film of pure gold. This continuous gold layer blocks the diffusion of H^+ ions into the SiO₂ network, but also protects it from exposure to water, allowing the application of continuous applied voltages. We then applied potentials of -1.5 and -2.0 V, which are not enough to produce solvated electrons but are high enough to create

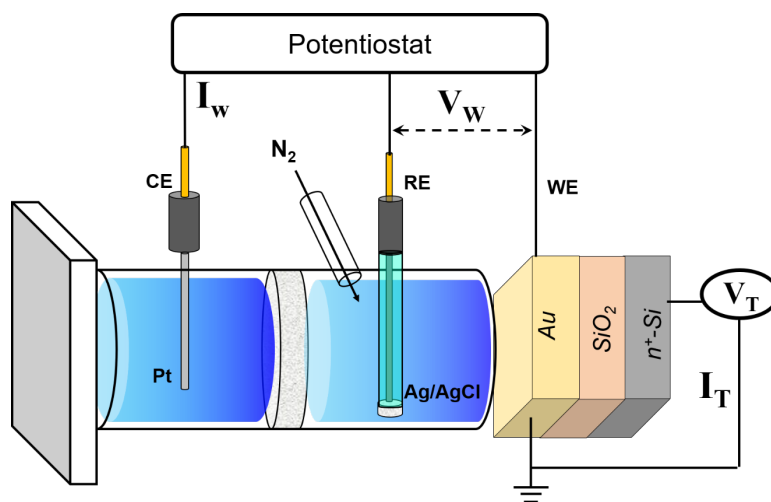


electrons at the gold surface, which may catalytically enhance hydrogenation of adsorbed N_2 molecules¹⁹⁻²⁰ Our hope, based on predictions by Norskov and Chorkendorf,²¹ was that this low flux of electrons reacts preferentially with N_2 molecules adsorbed on the gold surface rather than with each other. However, we were again foiled in our attempt to produce ammonia using either annealed or unannealed gold layers. These results are again shown in the histogram at the end, presumably again reflecting facial production of H_2 according to the Volmer reactions stated

earlier.

n^+ -Si/SiO₂/Au “Water Transistor”.¹³In a final attempt to minimize hydrogen evolution and enhance ammonia production, we converted the silicon-oxide-gold sandwich into a “water

transistor”, as shown in the figure on the right. In this transistor, potentials are separately applied between the silicon and gold electrodes of the device (V_T) and between the gold and reference electrode in solution (V_W). The key point is that the gold

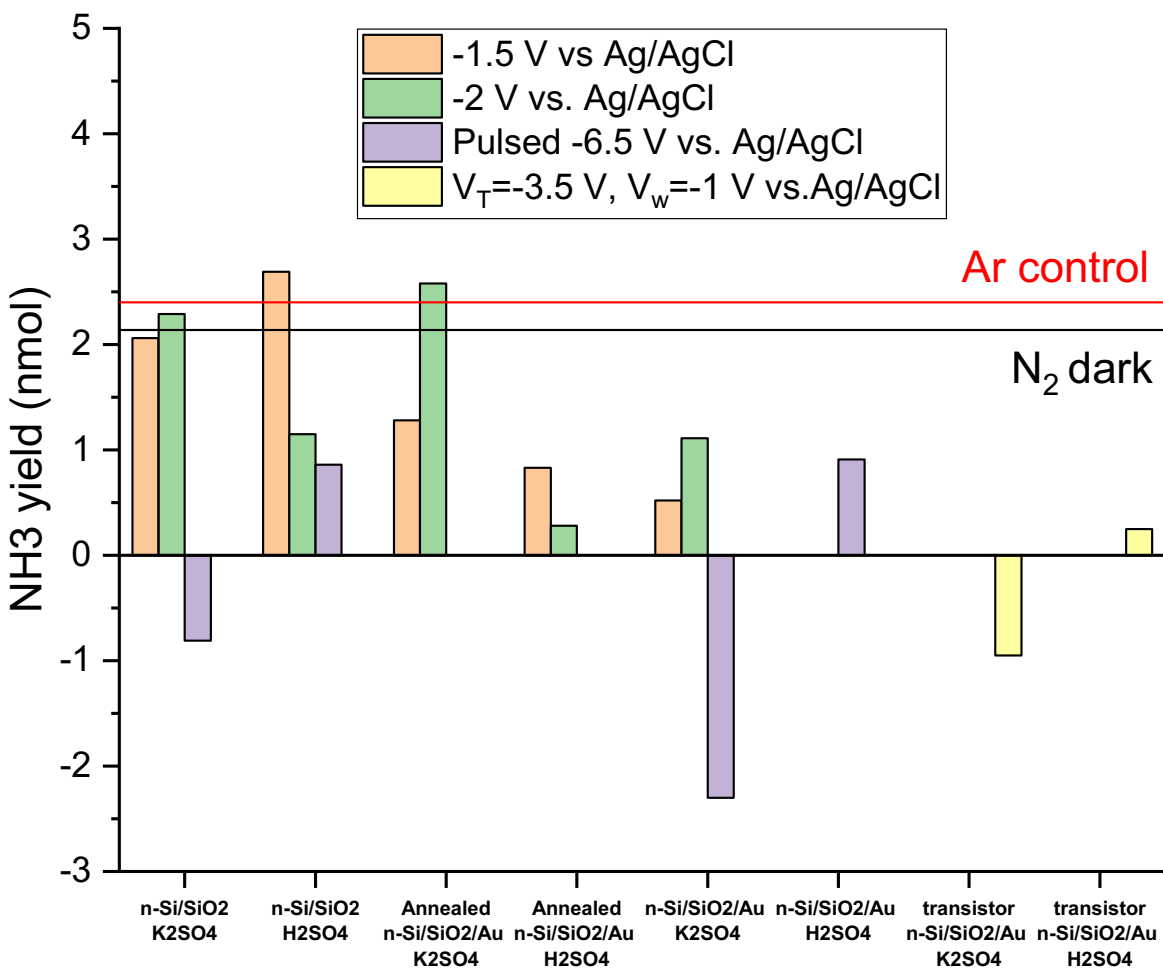


surface is at ground potential, severely inhibiting the production of H₂ at the electrode surface itself. The applied voltage V_T was set to -3.8 V, negative enough to produce solvated electrons. Despite these changes, we were still unable to record ammonia production above the control experiments, again likely because of the intense competition from H₂ evolution and possibly because of imperfect grounding of the thin gold layer. High voltage pulses instead of continuous applied voltages also did not produce more ammonia.

Future Approaches. We hope that these carefully constructed experiments provide the basis for future investigations. These devices still have great promise, but will require much greater efforts to minimize competition from hydrogen evolution and reaction with oxygen. In particular, direct spectroscopic measurements of solvated electrons via absorption and of hydrogen atoms via Raman experiments will help to tune the applied voltage, pulse duration, pH, electrolyte, and electrode parameters. These difficult measurements can be accompanied by

direct mass spectrometric measurements of H₂ production. A key test that we did not have time to perform is to place the electrochemical cell in a container of high pressure nitrogen to favor H attack on N₂ rather than H + H recombination. It may also be necessary to take advantage of recent developments in producing gold clusters that may react more favorably with adsorbed N₂ molecules. We are optimistic that future researchers will utilize our studies to guide their own work in the search for the sustainable production of ammonia from abundant resources.^{15, 21}

Summary of all Ammonia Production Measurements



Note: negative values indicate that the amount of ammonia produced was smaller than the blank comparison, a sample from the original solution taken before the voltage is applied.

II. Reductive Dehalogenation of 2-chloroethanol by Solvated Electrons Generated by Tunneling through High-k Dielectric Films

This summary of activities is abstracted from the M.S. thesis of Kirsten Louthan, a joint Hamers-Nathanson student who completed her M.S. work in 2018.

As noted above, the use of SiO₂ as a dielectric has some limitations, in part due to its small dielectric constant. This second aspect of our work focuses on increasing the tunneling current densities using high-k dielectrics, particularly HfO₂ (hafnium oxide, hafnia).

High-k dielectrics have been widely used in the microelectronics industry as gate dielectrics because

their high dielectric constant allows one to achieve

high interfacial capacitance (an important figure of merit for microelectronic devices) using insulators that are thicker than those of lower k materials such as SiO₂. However, a corollary is that if materials are compared a fixed thickness, then a then a high-k dielectric will yield a higher tunneling current compared with a low-k dielectric. This can be qualitatively understood by recognizing that electrons within a high-dielectric material are stabilized by polarization of the surrounding dielectric; this increased stability of the electron in the dielectric material also implies that the electron wave function decays more slowly in a high-k dielectric. Among high-k dielectrics, ZrO₂ and HfO₂ have received much attention because of their high dielectric constant ($\epsilon \sim 20$)²², compatibility common microelectronic materials,²³⁻²⁵ and ease of fabrication via atomic layer deposition (ALD)²⁶⁻²⁷.

Fabrication of high-k dielectric films:

We deposited ultra-thin (~5 nm thickness) films of HfO₂ using Atomic Layer Deposition (ALD),

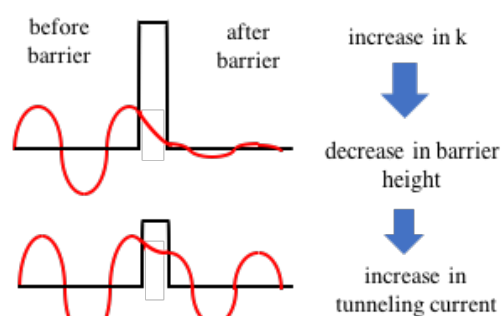
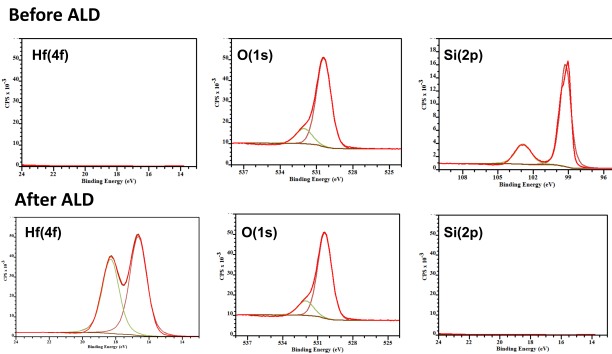


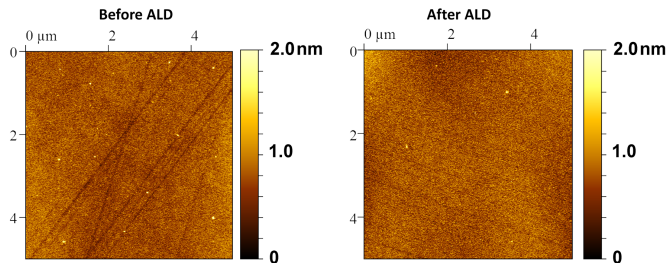
Figure 2: Relationship of tunneling probability to dielectric constant



using tetrakis(dimethylamino) hafnium and water as the hafnium and oxygen sources, respectively. X-ray photoelectron spectroscopy (XPS) analysis of films grown for different number of ALD cycles showed the expected disappearance of the Si(2p)

peaks from the underlying Si substrate and the stoichiometric addition of HfO₂. Ellipsometry and XPS studies were used to calibrate HfO₂ thickness vs. the number of ALD cycles, allowing us to prepare films of controlled and known thickness.

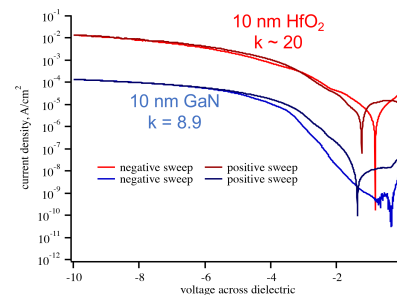
We assessed film morphology using atomic force microscopy (AFM). AFM before ALD (Figure 4a) shows the very flat conductive Si substrate; after growth, the surface appears highly



uniform, with only slightly increased roughness. These results demonstrate that ALD leads to highly uniform, conformal HfO₂ films, with a well defined growth rate of 1.1 Å/cycle.

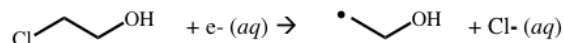
Electrical characterization:

To characterize the electrical performance of these films adjacent to an electrolyte solution, we compared cyclic voltammograms of two films with 100 mM phosphate buffer and a platinum counter electrode: a 10 nm GaN film ($\epsilon = 8.9$)²⁸ and a 10 nm HfO₂ film grown via ALD. The HfO₂ has a dielectric constant over twice of that of GaN and at the same physical thickness and bias conditions, we observed approximately 100x higher electron current at the same bias.



Solvated electron quantification:

To evaluate whether the observed current consists solvated electrons or related high-energy species, we investigated the reduction of 2-chloroethanol to chloride anion and directly characterized chloride via ion chromatography (IC), which proceeds via known reaction²⁹ through a one-electron reduction.



The concentration of 2-chloroethanol was carefully selected to favor 2-chloroethanol reduction over proton reduction and O₂ reduction using known rate constants¹⁶ (Table 1). Assuming a pH = 7.00 and a dissolved O₂ concentration dictated by Henry's Law at an atmospheric pressure of *ca.* 0.2 atm, we calculated that 200 mM 2-chloroethanol would out-compete both oxygen and proton reduction

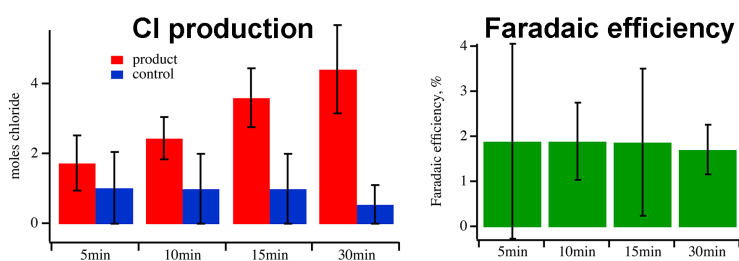
Table 1: Pseudo first-order rate constants

	Chemical species	2nd order k, M⁻¹s⁻¹	[reactant], M	pseudo 1st order k, s⁻¹	Preference for 2-chloroethanol
e- (aq)	H ⁺ (aq)	2.40 E10	1.00 E-7	2.40 E3	3.5 E5
e- (aq)	O ₂ (aq)	1.80 E10	2.6 E-4 (Henry's Law)	4.68 E6	179
e- (aq)	O ₂ (aq)	1.8 E10	4.49 E-6 (Butler ref.)	8.44 E4	9.94 E3
e- (aq)	ClEtOH (aq)	4.2 E8	0.200	8.40 E8	

For each electrolysis, an open-circuit control was collected before the electrolysis using the same

solution as the electrolysis. This controlled for the background chloride signal generated by an equilibrium between water and 2-chloroethanol³⁰ which produces a non-zero chloride background concentration.

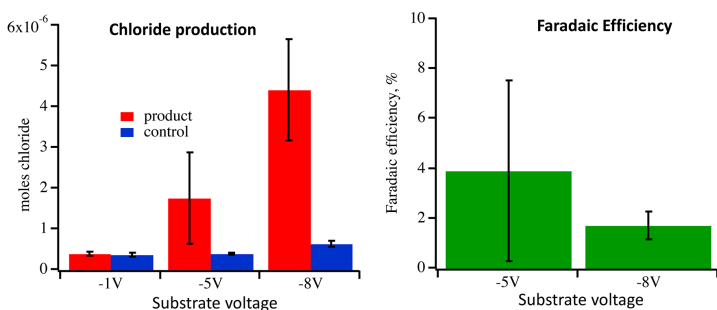
We first investigated at the dependence of chloride generated as a function of time for a 5 nm HfO₂ film with a -8 V bias on the silicon substrate in 100 mM phosphate buffer (50 mM K₂HPO₄ and 50 mM KH₂PO₄), 200 mM 2-chloroethanol and a platinum counter electrode in solution. For time < 15 minutes, the electrolysis is statistically indistinguishable from the control but for t ≥ 15



minutes the data show a net production of chloride over the control. When the data are normalized by the total charged passed and a Faradaic efficiency is

calculated, the data show similar Faradaic efficiencies at all time, which suggests a steady-state generation of solvated electrons. The similarity between the control and electrolysis for the earlier time points can be attributed to the equilibrium of 2-chloroethanol with water under basic conditions.

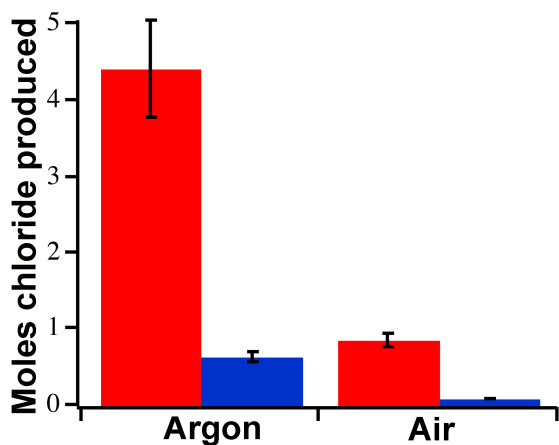
Influence of applied voltage: We also investigated the dependence of chloride production on



voltage by running a series of electrolyses on 5 nm HfO₂ films for 30 minutes while varying the voltage. The data net production of chloride for -5 and -8 V but not for -1 V. As expected from a tunneling model (which

predicts an exponential increase with applied voltage), the increase in chloride production is clearly supra-linear. More data are required to confirm an exponential dependence. As expected, the Faradaic efficiency is nearly constant.

Influence of electron scavengers: While the above data are all consistent with the



interpretation the solvated electrons are being produced, another way of testing is to intentionally introduce an electron scavenger. Oxygen gas reacts with the solvated electron at the diffusion-limited rate.^{16, 30} A direct comparison of chloride production in argon-purged and air-purge samples shows that the presence of oxygen greatly decreases the

production of chloride ion, by approximately a factor of 5. We believe this decrease in chloride production under air-purged conditions occurs because O₂ is in competition with 2-chloroethanol. These data strongly support the idea that the production of chloride is a result of solvated electron formation, rather than traditional electrochemical reduction on the electrode surface.

Conclusions:

In this work we show a novel application for high-k dielectrics to produce aqueous electrons at low voltage. This has great potential applications in wastewater treatments in dehalogenation of dangerous pesticides³¹ and synthesis of important products, including ammonia from atmospheric nitrogen⁴. Each year, 150 million tons of ammonia are produced, requiring temperatures of 300-550°C and pressures of 150-250 atm³², releasing 200 million tons of atmospheric CO₂ in the process³³. This type of electrochemical synthesis offers an alternate synthetic route and has the further advantage of relying on a solution-phase mechanism, enabling any dielectric with sufficiently high current density to be used. Many high-k dielectrics are well-studied materials^{25, 34-35}, and some are already being developed for reactions in aqueous conditions^{25, 34-35}, although this is the first report of using them as for high tunneling, rather than low tunneling currents.

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