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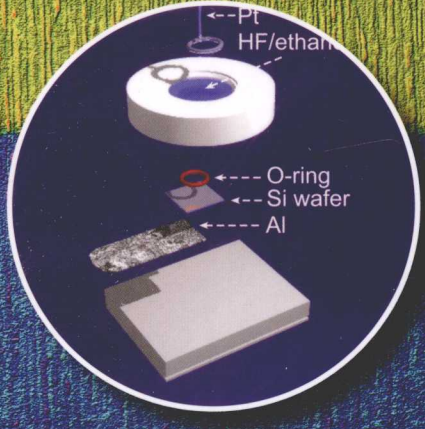
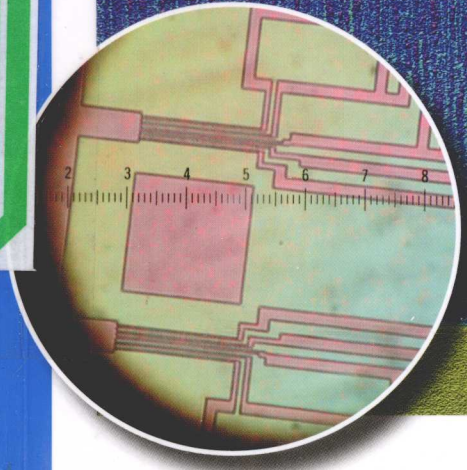
Porous Silicon in Practice

Preparation, Characterization and Applications





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Preface

This book is written for the beginner–someone who has no prior training in the field. It began as a series of summer tutorial lectures that I gave to my research group to familiarize them with the preparation and characterization of porous silicon. I found that the traditional undergraduate chemistry, biochemistry, bioengineering, physics, or materials science curriculum does not prepare one to work with porous silicon–most of my students would come into the group with no understanding of the electrochemical methods needed to carry out its synthesis, little appreciation for the fundamental semiconductor physics, electronics, chemistry, and optics principles needed to exploit its properties, and a sizable fear of the hydrofluoric acid used in its preparation. The tutorials resulted from my frustration that the basic conceptual and experimental "tricks of the trade" were not being passed from one student to the next. My goal was to provide my students with all that I thought they needed to know to get started in their research projects and survive the grilling of their second year oral committee. I provided laboratory "homework" experiments to get the students comfortable with the equipment and the techniques we use. The experiments in Chapters 1–5 are a direct result of these homework assignments. They are structured, step-by-step procedures with well-characterized results. I wrote them to allow me to correct obvious errors in laboratory technique or understanding before the student embarked on his or her independent research project, where errors are not as easily caught and carry significant consequences. The large increase in interest in porous silicon in the past few years, and the numerous email messages I have been receiving from students in groups around the world, asking me for details of our synthetic and optical analysis methods, gives me hope that more than my own research group members will make use of this material.

In the summer of 2004 I was fortunate to meet Esther Levy from Wiley-VCH, who, along with Martin Ottmar, encouraged me to convert my tutorial into a book. I thank them and the rest of the publishing team at Wiley-VCH for their patience during the several years spanning the writing and production of this work.

Many of my coworkers and collaborators contributed the ideas, concepts, and images that make up a large part of this book. In particular, I thank Gordon M. Miskelly, Giuseppe Barillaro, Andrea Potocny, Manuel Orosco, Sophia Oller, Ester Segal, M. Shaker Salem, Yukio H. Ogata, Stephanie Pace, Frederique Cunin, Jean-Marie Devoiselle, Luo Gu, Joseph Lai, Emily Anglin, Beniamino Sciacca, Michelle Y. Chen, Sara Alvarez, Anne M. Ruminski, Adrian Garcia Sega, and Vinh Diep.

Finally, I thank my family for putting up with the late nights, early mornings, and missed dinner appointments they suffered as I went through this process.

La Jolla
August 2011

Michael J. Sailor

Contents

Preface *XI*

1 **Fundamentals of Porous Silicon Preparation** *1*
1.1 Introduction *1*
1.2 Chemical Reactions Governing the Dissolution of Silicon *2*
1.2.1 Silicon Oxides and Their Dissolution in HF *3*
1.2.2 Silicon Oxides and Their Dissolution in Basic Media *3*
1.2.3 Silicon Hydrides *4*
1.3 Experimental Set-up and Terminology for Electrochemical Etching of Porous Silicon *5*
1.3.1 Two-Electrode Cell *6*
1.3.2 Three-Electrode Cell *6*
1.4 Electrochemical Reactions in the Silicon System *7*
1.4.1 Four-Electron Electrochemical Oxidation of Silicon *8*
1.4.2 Two-Electron Electrochemical Oxidation of Silicon *9*
1.4.3 Electropolishing *10*
1.5 Density, Porosity, and Pore Size Definitions *11*
1.6 Mechanisms of Electrochemical Dissolution and Pore Formation *13*
1.6.1 Chemical Factors Controlling the Electrochemical Etch *16*
1.6.2 Crystal Face Selectivity *18*
1.6.3 Physical Factors Controlling the Electrochemical Etch *18*
1.7 Resume of the Properties of Crystalline Silicon *19*
1.7.1 Orientation *19*
1.7.2 Band Structure *20*
1.7.3 Electrons and Holes *21*
1.7.4 Photoexcitation of Semiconductors *22*
1.7.5 Dopants *23*
1.7.6 Conductivity *24*
1.7.7 Evolution of Energy Bands upon Immersion in an Electrolyte *24*
1.7.8 Charge Transport at p-Type Si Liquid Junctions *26*

1.7.9 Idealized Current–Voltage Curve at p-Type Liquid Junctions *26*
1.7.10 Energetics at n-Type Si Liquid Junctions *28*
1.7.11 Idealized Current–Voltage Curve at n-type Liquid Junctions *28*
1.8 Choosing, Characterizing, and Preparing a Silicon Wafer *28*
1.8.1 Measurement of Wafer Resistivity *29*
1.8.2 Cleaving a Silicon Wafer *34*
1.8.3 Determination of Carrier Type by the Hot-Probe Method *36*
1.8.4 Ohmic Contacts *36*
1.8.4.1 Making an Ohmic Contact by Metal Evaporation *39*
1.8.4.2 Making an Ohmic Contact by Mechanical Abrasion *40*
References *40*

2 Preparation of Micro-, Meso-, and Macro-Porous Silicon Layers *43*
2.1 Etch Cell: Materials and Construction *43*
2.2 Power Supply *44*
2.3 Other Supplies *48*
2.4 Safety Precautions and Handling of Waste *48*
2.5 Preparing HF Electrolyte Solutions *50*
2.6 Cleaning Wafers Prior to Etching *51*
2.6.1 No Precleaning *51*
2.6.2 Ultrasonic Cleaning *51*
2.6.3 RCA Cleaning *52*
2.6.4 Removal of a Sacrificial Porous Layer with Strong Base *52*
2.7 Preparation of Microporous Silicon from a p-Type Wafer *53*
2.8 Preparation of Mesoporous Silicon from a p^{++}-Type Wafer *57*
2.9 Preparation of Macroporous, Luminescent Porous Silicon from an n-Type Wafer (Frontside Illumination) *59*
2.9.1 Power Supply Limitations *63*
2.10 Preparation of Macroporous, Luminescent Porous Silicon from an n-Type Wafer (Back Side Illumination) *64*
2.11 Preparation of Porous Silicon by Stain Etching *68*
2.12 Preparation of Silicon Nanowire Arrays by Metal-Assisted Etching *73*
References *75*

3 Preparation of Spatially Modulated Porous Silicon Layers *77*
3.1 Time-Programmable Current Source *78*
3.1.1 Time Resolution Issues *79*
3.1.2 Etching with an Analog Source *80*
3.1.3 Etching with a Digital Source *82*
3.2 Pore Modulation in the *z*-Direction: Double Layer *83*
3.3 Pore Modulation in the z-Direction: Rugate Filter *83*
3.3.1 Tunability of the Rugate Spectral Peak Wavelength *88*
3.3.2 Width of the Spectral Band *92*

3.4 More Complicated Photonic Devices: Bragg Stacks, Microcavities, and Multi-Line Spectral Filters *94*
3.4.1 Bragg Reflector *96*
3.4.2 Multiple Spectral Peaks-"Spectral Barcodes" *100*
3.5 Lateral Pore Gradients (in the x–y Plane) *104*
3.6 Patterning in the x–y Plane Using Physical or Virtual Masks *108*
3.6.1 Physical Masking Using Photoresists *109*
3.6.2 Virtual Masking Using Photoelectrochemistry *112*
3.7 Other Patterning Methods *114*
References *114*

4 Freestanding Porous Silicon Films and Particles *119*
4.1 Freestanding Films of Porous Silicon-"Lift-offs" *120*
4.2 Micron-scale Particles of Porous Silicon by Ultrasonication of Lift-off Films *120*
4.3 Core–Shell (Si/SiO_2) Nanoparticles of Luminescent Porous Silicon by Ultrasonication *126*
References *130*

5 Characterization of Porous Silicon *133*
5.1 Gravimetric Determination of Porosity and Thickness *134*
5.1.1 Errors and Limitations of the Gravimetric Method *137*
5.2 Electron Microscopy and Scanned Probe Imaging Methods *138*
5.2.1 Cross-Sectional Imaging *138*
5.2.2 Plan-View (Top-Down) Imaging *139*
5.3 Optical Reflectance Measurements *139*
5.3.1 Instrumentation to Collect Reflectance Data *139*
5.3.1.1 Reflectance Optics *140*
5.3.1.2 Wavelength Calibration *142*
5.3.2 Principles of Fabry–Pérot Interference *143*
5.3.3 Analyzing Fabry–Pérot Interference Spectra by Fourier Transform: the RIFTS Method *150*
5.3.3.1 Preparation of Spectrum for Fast Fourier Transform *151*
5.3.3.2 Interpretation of the Fast Fourier Transform *153*
5.3.4 Thickness and Porosity by the Spectroscopic Liquid Infiltration Method (SLIM) *154*
5.3.4.1 Bruggeman Effective Medium Approximation *155*
5.3.4.2 Determination of Thickness and Porosity by SLIM *156*
5.3.4.3 Determination of Index of Refraction of the Porous Skeleton *156*
5.3.4.4 Effect of Skeleton Index on Porosity Determined by SLIM *158*
5.3.5 Comparison of Gravimetric Measurement with SLIM for Porosity and Thickness Determination *159*
5.3.6 Analysis of Double-Layer Structures Using RIFTS *162*

5.4 Porosity, Pore size, and Pore Size Distribution by Nitrogen Adsorption Analysis (BET, BJH, and BdB Methods) *167*
5.5 Measurement of Steady-State Photoluminescence Spectra *170*
5.5.1 Origin of Photoluminescence from Porous Silicon *170*
5.5.1.1 Tunability of the Photoluminescence Spectrum *171*
5.5.1.2 Mechanisms of Photoluminescence *171*
5.5.2 Instrumentation to Acquire Steady-State Photoluminescence Spectra *173*
5.6 Time-Resolved Photoluminescence Spectra *173*
5.6.1 Long, Nonexponential Excited State Lifetimes *173*
5.6.2 Influence of Surface Traps *175*
5.7 Infrared Spectroscopy of Porous Silicon *176*
5.7.1 Characteristic Group Frequencies for Porous Silicon *176*
5.7.2 Measurement of FTIR Spectra of Porous Silicon *178*
5.7.2.1 Transmission Mode Measurement Using the Standard Etch Cell *179*
References *181*

6 Chemistry of Porous Silicon *189*
6.1 Oxide-Forming Reactions of Porous Silicon *190*
6.1.1 Temperature Dependence of Oxidation Using Gas-Phase Oxidants *190*
6.1.2 Thermal (Air) Oxidation *191*
6.1.3 Ozone Oxidation *192*
6.1.4 High-Pressure Water Vapor Annealing *193*
6.1.5 Oxidation in Aqueous Solutions *193*
6.1.5.1 Aqueous Oxidation Induced by Cationic Surfactants *194*
6.1.6 Electrochemical Oxidation in Aqueous Mineral Acids *194*
6.1.7 Oxidation by Organic Species: Ketones, Aldehydes, Quinones, and Dimethylsulfoxide *195*
6.1.8 Effect of Chemical Oxidation on Pore Morphology *196*
6.2 Biological Implications of the Aqueous Chemistry of Porous Silicon *198*
6.3 Formation of Silicon–Carbon Bonds *200*
6.3.1 Thermal Hydrosilylation to Produce Si–C Bonds *200*
6.3.2 Working with Air- and Water-Sensitive Compounds – Schlenk Line Manipulations *201*
6.3.3 Classification of Surface Chemistry by Contact Angle *203*
6.3.4 Microwave-Assisted Hydrosilylation to Produce Si–C Bonds *204*
6.3.5 Chemical or Electrochemical Grafting to Produce Si–C Bonds *206*
6.4 Thermal Carbonization Reactions *208*
6.4.1 Thermal Degradation of Acetylene to form "Hydrocarbonized" Porous Silicon *208*

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6.4.2 Thermal Degradation of Polymers to Form "Carbonized" Porous Silicon *209*
6.5 Conjugation of Biomolecules to Modified Porous Silicon *211*
6.5.1 Carbodiimide Coupling Reagents *211*
6.5.2 Attachment of PEG to Improve Biocompatibility *212*
6.5.3 Biomodification of "Hydrocarbonized" Porous Silicon *213*
6.5.4 Silanol-Based Coupling to Oxidized Porous Silicon Surfaces *215*
6.6 Chemical Modification in Tandem with Etching *217*
6.7 Metallization Reactions of Porous Silicon *218*
References *219*

Appendix A1. Etch Cell Engineering Diagrams and Schematics *229*
Standard or Small Etch Cell-Complete *229*
Standard Etch Cell Top Piece *230*
Small Etch Cell Top Piece *231*
Etch Cell Base (for Either Standard or Small Etch Cell) *232*
Large Etch Cell-Complete *232*
Large Etch Cell Top Piece *233*
Large Etch Cell Base *233*

Appendix A2. Safety Precautions When Working with Hydrofluoric Acid *235*
Hydrofluoric Acid Hazards *235*
First Aid Measures for HF Contact *236*
Note to Physician *238*
HF Antidote Gel *239*
Further Reading 239

Appendix A3. Gas Dosing Cell Engineering Diagrams and Schematics *241*
Gas Dosing Cell Top Piece *242*
Gas Dosing Cell Middle Piece *243*
Gas Dosing Cell Bottom Piece *244*

Index *245*

1
Fundamentals of Porous Silicon Preparation

1.1
Introduction

Porous silicon was accidentally discovered by the Uhlirs, a husband and wife team working at Bell Laboratories in the mid 1950s. They were trying to develop an electrochemical method to machine silicon wafers for use in microelectronic circuits. Under the appropriate electrochemical conditions, the silicon wafer did not dissolve uniformly as expected, but instead fine holes appeared, propagating primarily in the <100> direction in the wafer. Since this did not provide the smooth polish desired, the curious result was reported in a Bell labs technical note [1], and then the material was more or less forgotten. In the 1970s and 1980s a significant level of interest arose because the high surface area of porous silicon was found to be useful as a model of the crystalline silicon surface in spectroscopic studies [2–5], as a precursor to generate thick oxide layers on silicon, and as a dielectric layer in capacitance-based chemical sensors [6].

Interest in porous silicon, and in particular in its nanostructure, exploded in the early 1990s when Ulrich Goesele at Duke University identified quantum confinement effects in the absorption spectrum of porous silicon, and almost simultaneously Leigh Canham at the Defense Research Agency in England reported efficient, bright red–orange photoluminescence from the material [7, 8]. The quantum confinement effects arise when the pores become extensive enough to overlap with each other, generating nanometer-scale silicon filaments. As expected from the quantum confinement relationship [9], the red to green color of photoluminescence occurs at energies that are significantly larger than the bandgap energy of bulk silicon (1.1 eV, in the near-infrared).

With the discovery of efficient visible light emission from porous silicon came a flood of work focused on creating silicon-based optoelectronic switches, displays, and lasers. Problems with the material's chemical and mechanical stability, and its disappointingly low electroluminescence efficiency led to a waning of interest by the mid 1990s. In the same time period, the unique features of the material – large surface area, controllable pore

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sizes, convenient surface chemistry, and compatibility with conventional silicon microfabrication technologies–inspired research into applications far outside optoelectronics. Many of the fundamental chemical stability problems have been overcome as the chemistry of the material has matured, and various biomedical [10–18] sensor, optics, and electronics applications have emerged [10].

Porous silicon is generated by etching crystalline silicon in aqueous or non-aqueous electrolytes containing hydrofluoric acid (HF). This book describes basic electrochemical and chemical etching experiments that can be used to make the main types and structures of porous silicon. Beginning with measurement of wafer resistivity, the experiments are intended for the newcomer to the field, written in the form of detailed procedures, including sources for the materials and equipment. Experiments describing methods for characterization and key chemical modification reactions are also provided. The present chapter gives an overview of fundamentals that are a useful starting point to understand the theory underlying the experiments in the later chapters.

1.2 Chemical Reactions Governing the Dissolution of Silicon

The formation of porous silicon involves reactions of Si–Si, Si–H, Si–O, and Si–F bonds at the surface of the silicon crystal. The relative strengths of these bonds, obtained from thermodynamic measurements of molecular analogues, are given in Table 1.1. While one might think that the strengths of these bonds would determine the relative stability of each species on a silicon surface, the electronegativity of the elements plays a much more important role. Si–H and Si–C species tend to passivate the silicon surface in aqueous solutions, while the Si–F bond is highly reactive. Electronegative elements such as O and F form more polar Si–X bonds, making the silicon

Table 1.1 Enthalpies of some Si–X bonds.

Compound	Bond	Enthalpy, kcal mol^{-1}
$Me_3Si–SiMe_3$	Si–Si	79
$Me_3Si–CH_3$	Si–C	94
$Me_3Si–H$	Si–H	95
$Me_3Si–OMe_3$	Si–O	123
$Me_3Si–F$	Si–F	158

Taken from Robin Walsh, Gelest Catalog: www.gelest.com

atom susceptible to nucleophilic attack. The surface of freshly prepared porous silicon is covered with a passivating layer of Si–H bonds, with minor quantities of Si–F and Si–O species.

1.2.1 Silicon Oxides and Their Dissolution in HF

Silicon is thermodynamically unstable in air or water, and it reacts spontaneously to form an oxide layer. The oxide can be nonstoichiometric and hydrated to various degrees, though the simple empirical formula is silicon dioxide, SiO_2 (Equation 1.1). SiO_2 is a key thermodynamic sink in the silicon system.

$$Si + O_2 \rightarrow SiO_2 \tag{1.1}$$

SiO_2 is an electrical insulator that forms passivating films on crystalline silicon; preparation of porous silicon thus requires an additive in the solution to dissolve the oxide and allow electrochemical oxidation to continue. The Si–F bond is the only bond stronger than Si–O, and it is the Si–F bond enthalpy that drives the main chemical dissolution reaction used to make porous silicon. In the presence of aqueous HF, SiO_2 spontaneously dissolves as SiF_6^{2-} (Equation 1.2).

$$SiO_2 + 6\ HF \rightarrow SiF_6^{2-} + 2\ H^+ + 2\ H_2O \tag{1.2}$$

The reaction of SiO_2 with HF is a common industrial reaction. It is used to prepare frosted glass from plate glass and to remove SiO_2 masking layers in the processing of silicon wafers in microelectronics. The silicon hexafluoride ion (SiF_6^{2-}) is a stable dianion that is highly soluble in water. Thus fluoride is the most important additive used in the preparation of porous silicon, dissolving the insulating oxide that would otherwise shut down the electrochemical corrosion reaction.

1.2.2 Silicon Oxides and Their Dissolution in Basic Media

In the absence of fluoride ion, SiO_2 on the surface of a silicon wafer protects the underlying silicon from further oxidation. While this is true in acidic or neutral aqueous solutions, in basic solutions hydroxide ions attack and dissolve the oxide by Equation 1.3:

$$SiO_2 + 2\ OH^- \rightarrow [SiO_2(OH)_2]^{2-} \tag{1.3}$$

The net dissolution reaction for silicon in basic media then becomes:

$$Si + 2\ OH^- + 2\ H_2O \rightarrow [SiO_2(OH)_2]^{2-} + 2\ H_2 \tag{1.4}$$

The reaction represented by Equation 1.3 is highly simplified. The species $[SiO_2(OH)_2]^{2-}$, the doubly protonated form of silicic acid, is only one of many water-soluble forms of silicon oxide. The fundamental oxide-containing unit is the SiO_4^{4-} tetrahedron, known as the orthosilicate ion [11]. Orthosilicate itself is highly basic, and in aqueous solutions it is never present as the naked SiO_4^{4-} ion. The fully protonated species is orthosilicic acid, $Si(OH)_4$, and this is the generic formula that is often presented in the literature to indicate all the water-soluble forms of silicic acid. The first ionization constant (pK_a) of $Si(OH)_4$ is about 10, and the second (pK_a) is around 12. Thus the $[SiO_2(OH)_2]^{2-}$ ion depicted in Equation 1.3 is only present in highly basic (pH > 12) solutions. In neutral or acidic solutions, $Si(OH)_4$ is the predominant monomeric form.

When the solution concentration of $Si(OH)_4$ is sufficiently large, silicic acid condenses into oligomers. Various "polysilicic acids" with the general formula $[SiO_x(OH)_{4-2x}]_n$, where $2 > x > 0$, are present in solution [11]. In neutral or acidic solutions these oligomers can condense to the point of precipitation, essentially the reverse of Equation 1.3:

$$Si(OH)_4 \rightarrow SiO_2 + 2\ H_2O \tag{1.5}$$

The reaction represented in Equation 1.5 is the key reaction in the "sol–gel" process, often used to prepare colloids, films, or monoliths of porous silica from solution precursors [12]. The insolubility of SiO_2 in acidic solutions explains why elemental silicon does not corrode appreciably at pH < 7; the oxide provides a protective, passivating layer. The same is not true in basic solutions; here the solubility of silicon oxide drives silicon oxidation and dissolution by Equation 1.4. The high surface area and relatively strained nature of Si–Si bonds in porous silicon make the reaction with hydroxide ion quite rapid. In Chapter 2 we will employ this reaction (using aqueous KOH) to dissolve a porous silicon layer in order to determine its porosity. The Si–Si bonding in bulk silicon is less strained, and bulk silicon dissolves more slowly in basic solutions. In these and other situations where the oxide is soluble, dissolution of silicon becomes limited by surface Si–H species.

1.2.3 Silicon Hydrides

The reaction of silicon with water should be analogous to the reaction of metallic sodium in water; elemental silicon is electropositive enough to spontaneously liberate hydrogen from water. However, silicon does not dissolve in acidic solutions, even if the solution contains fluoride ion to remove the passivating SiO_2 layer. Although thermodynamically feasible, dissolution of silicon in aqueous HF is slow unless strong oxidizing agents (such as O_2 or NO_3^-) are present in the solution, or unless the oxidation reaction is driven by electrochemistry. The reason is that corrosion becomes kinetically limited by the passivating nature of surface hydrides.

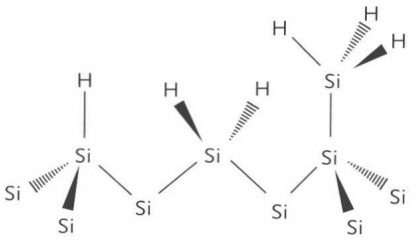

Figure 1.1
Hydrides on the porous silicon surface. The freshly etched surface of porous silicon is terminated primarily with hydride species. Residual oxides or fluorides are removed by the HF electrolyte. Three types of surface hydrides are depicted: SiH, SiH_2, and SiH_3.

When silicon is chemically or electrochemically etched in HF-containing solutions, the exposed silicon surface becomes terminated with H atoms (Figure 1.1). The mechanism of this reaction is described in more detail later in this chapter. The surface Si–H species are not readily removed by acid, and they must be oxidized to allow the silicon corrosion reaction to continue. In alkaline solutions, OH^- is able to attack these species because it is a good nucleophile. Nucleophilic attack is an important reaction in the silicon system, and it is discussed in more detail in Chapter 6. The Si–H species on porous silicon can also be removed by the action of a cationic surfactant, which polarizes the surface and induces nucleophilic attack by water, even in acidic solutions [13]. This reaction is also discussed in Chapter 6.

1.3 Experimental Set-up and Terminology for Electrochemical Etching of Porous Silicon

In an electrochemical reaction, two electrodes are needed. One supplies electrons to the solution (the cathode) and the other removes electrons from the solution (the anode). It is important to keep in mind that the two electrodes are required to maintain charge neutrality and to complete the electrical circuit. Regardless of the oxidation or reduction reactions occurring at the electrodes, you cannot perform electrochemistry if you do not complete the circuit. This means that at least two reactions are occurring simultaneously in an electrochemical cell, the anode (oxidation) reaction and the cathode (reduction) reaction. Electrochemists refer to these as "half-reactions." A schematic of a two-electrode cell for etching silicon, with the relevant half-reactions, is shown in Figure 1.2.

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