Chapter 2

Macroporous Silicon as a Model System for Silicon Wire Array Solar Cells

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2.1 Abstract

Macroporous silicon samples have been investigated in photoelectrochemical cells, and their behavior has been compared to that of conventional, planar, Si/liquid junctions. The liquid electrolyte junction provided a conformal contact to the macroporous Si, and allowed assessment of the trade-offs between increased surface area and decreased carrier collection distances in such systems relative to the behavior of planar semiconductor/ liquid photoelectrochemical junctions. The electrolyte contained the dimethylferrocene/ dimethylferrocenium redox system in methanol because this system has been shown previously to produce bulk recombination-diffusion limited contacts at planar Si(100) electrodes under 100 mW cm⁻² of simulated air mass 1.5 illumination. Introduction of a network of ~2-3 µm diameter, ~80 µm long pores into the Si was found to slightly reduce the short-circuit photocurrent density and the open-circuit voltage of the system, but energy-conversion efficiencies in excess of 10% were nevertheless obtained from such samples. This system therefore validates the concept of using interpenetrating networks to produce efficient solar energy conversion devices in systems that do not have long carrier collection distances.

2.2 Introduction

A key constraint in planar solar cell designs is that the minority-carrier collection length, including both the diffusion length and the width of the electric-field region, must be comparable to, or preferably should exceed, the absorption depth of the material for the relevant photon energies of the solar spectrum. In typical planar-junction devices, this restriction imposes a purity related, and therefore an associated cost-related, constraint on the absorber material, because the diffusion length in the absorber must be sufficient to allow photogenerated carriers to arrive in the space-charge region, where they can be effectively separated and ultimately collected at the external contacts.

One approach to enable the use of cheaper materials in solar cells involves orthogonalization of the directions of light absorption and charge-carrier collection. For example, in an oriented array of semiconductor nanorods having radial p-n junctions, the light can be absorbed along the long axis of the rod, whereas the charge carriers can diffuse a short distance radially to the junction (Figure 2.1). In this design, devices exhibiting high energy-conversion efficiencies can in principle be produced from an absorber material that has a much smaller diffusion length than that needed for high efficiency in a planar solar cell configuration. Specifically, an analytical study of the governing generation, transport, and recombination equations has shown that high efficiencies can be maintained in oriented rod array solar cells provided that the diffusion length in the material is comparable to the radius of the rod.¹ Materials with diffusion lengths as low as 100 nm, or even 10 nm, can thus in principle be used in efficient solar cells, provided that the rods are sufficiently small in diameter. The principle applies to



Figure 2.1. Schematic drawing of the difference between a traditional planar solar cell and a wire array solar cell. In the planar cell, the minority carrier diffusion length (L_p) must be comparable to the absorption length $(1/\alpha)$. In the wire array cell, the minority carriers can diffuse radially to the junction, while light is still absorbed along the axial dimension of the wire.

indirect band-gap semiconductors, such as Si, for which an increased diffusion length is associated with an increased purity and cost of the absorber material, and applies to earthabundant, inexpensive materials, such as Fe_2O_3 ,² that are generally nonstoichiometric and therefore have short diffusion lengths.

The nanorod-based solar cell design does, however, involve a design rule trade-off. Relaxation of the constraint on the purity of the absorber material comes at the expense of a larger surface area per unit of projected area of the device. To obtain high energyconversion efficiencies, analytical simulations have shown that the rod array device design requires very low surface recombination velocities as well as extremely low junction recombination rates.¹ Increased carrier collection has been observed previously for porous n-GaP and n-SiC photoelectrodes in anodic photocorrosion processes,³⁻⁵ but there is no information on whether the open-circuit voltage of stable, regenerative photoelectrochemical cells is degraded as a result of the introduction of porosity to the electrode material. To date, photovoltaic cells have been made from nanorods of CdSe, CdTe, Fe₂O₃, TiO₂, and ZnO, but demonstrated efficiencies in such systems are less than 5%, and typically less than 1-2%.⁶⁻¹³ Although the modest observed energy-conversion efficiencies are believed to primarily reflect poor light harvesting efficiencies in the structures prepared to date, it is not clear whether the observed efficiencies are also influenced by too low diffusion lengths for the nanorod radii employed to date, excessive junction or surface recombination, and/or whether the analytical description of this device design has omitted a key physical process that prevents efficient photovoltaic performance from being obtained through the wire array approach.

In this work, we have investigated a model light absorption and charge-carrier orthogonalization device implementation using macroporous Si as the light-absorbing medium. Macroporous Si can be made from bulk Si wafers, whose purity and diffusion length can be controlled, and measured, prior to fabrication of the pillared, light absorbing, phase.¹⁴ The junctions have been made using CH₃OH that contains the 1,1'- dimethylferrocenenium/ferrocene (Me₂Fc^{+/0}) redox couple, because such liquid junctions conform to the morphology of the pillared light absorber. Additionally, the CH₃OH-Me₂Fc^{+/0} system has been shown to create an inversion layer on n-type Si(100) surfaces, producing an in-situ p⁺-n junction structure having sufficiently low interfacial and junction recombination rates to produce bulk diffusion-limited open-circuit voltages of \sim 670 mV under 100 mW cm⁻² of air mass (AM) 1.5 illumination.^{15,16}

Porous silicon can be fabricated from a wide variety of bulk Si materials.^{14,17-23} Although microporous silicon has been studied more extensively due to its potential applications to optoelectronics and sensors,²⁴⁻²⁹ macroporous silicon is better-suited as a model system for evaluating the orthogonalized photovoltaic device design principles because the geometric structure of macroporous Si more closely resembles that of free-By etching a planar, bulk Si substrate in HF(aq) under back-side standing Si rods. illumination, n-type Si can be etched to produce long, straight-walled, uniform pores having micron-sized dimensions.^{14,17,18,20,23} The pore formation in n-type silicon is believed to occur through a hole-limited silicon dissolution process.^{14,17,19-22,28,30,31} As pores develop in the sample, holes generated at the back diffuse through the silicon and are preferentially harvested at the pore tips, where the tip curvature causes the electric field to be the largest.^{28,30,31} The space between the pores is believed to be completely depleted, inhibiting holes from diffusing between the pores to dissolve the sidewalls.^{14,28} The pore diameter and spacing can be controlled by the current density of the etching, the applied voltage, and the doping of the sample, while the pore length can be controlled independently by adjusting the etching time.²⁸ Thus, samples having different pore lengths, but similar pore structures, can be fabricated and used as working electrodes in photoelectrochemical energy conversion devices.

The behavior of silicon photoelectrodes has been explored extensively.^{15,32-41} Systems using methanol as the solvent, LiClO₄ as the supporting electrolyte, and ferrocene/ferrocenium derivatives have achieved energy conversion efficiencies of 10-14%.^{32,36,37} The highest efficiencies (14.1%) have been achieved using thin-layer twoelectrode photoelectrochemical solar cells, which minimize many of the mass transport, resistance, and optical absorption issues encountered in more traditional three-electrode, potentiostatically controlled, electrochemical systems.³² The thin-layer set-up is not wellsuited for reproducibly testing a large number of different types of porous samples, however, so the more common three-electrode cell was used for the experiments described herein. Efficiencies of 7.8% have been previously observed using this cell geometry for polished, planar n-Si(100) samples in contact with (1hydroxy)ethylferrocene^{+/0} in CH₃OH.³⁷ Higher efficiencies have been obtained by etching the samples to reduce optical reflection losses, and by use of more highly doped substrates to minimize bulk recombination. Dimethylferrocene^{+/0} (Me₂Fc^{+/0}) in methanol is known to form large barrier heights (~1 V) in contact with n-Si surfaces.⁴² These large barrier heights have been shown to result in low surface recombination, due to the low concentration of majority carriers at the surface of the sample.¹⁶ In addition, some of the surface passivation persists after the sample is removed from solution, implying that the surface is modified with methoxy groups as a result of exposure to the solution.¹⁶ These characteristics make the CH₃OH-Me₂Fc^{+/0} system an attractive choice for the comparison of behavior of macroporous Si and planar Si photoelectrodes. Samples of macroporous Si with varying pore lengths have been investigated, and the results have been compared to the behavior of planar (100)- and (110)-oriented silicon samples in the same electrolyte solution. In addition, cyclic voltammetry has been used to evaluate the internal junction area and carrier transport distances of the macroporous Si photoelectrodes relative to those of planar Si samples.

2.3 Experimental

2.3.1 Reagents

Methanol (BakerDry, Baker, Phillipsburg, NJ), sodium dodecylsulfate (SDS) (Sigma-Aldrich, St. Louis, MO), 49% (27 M) HF(aq) (Transene, Inc., Danvers, MA), and buffered HF(aq) (Transene) were used without further purification. Water (18 M Ω cm resistivity) was obtained from a Barnstead Nanopure system. Lithium perchlorate, LiClO₄ (Sigma-Aldrich), was fused under vacuum and stored under an inert atmosphere until use. Me₂Fc (Sigma-Aldrich) was sublimed at ~ 45 °C under vacuum and was stored under an inert atmosphere until use. Dimethylferrocenium tetrafluoroborate (Me₂FcBF₄) was synthesized from Me₂Fc by addition of excess HBF₄ in the presence of 0.5 equivalents of benzoquinone. The reaction was conducted under argon in an ice-water bath. The resulting solid was dried under vacuum and stored in an inert atmosphere. Me₂Fc and Me₂FcBF₄ were stored in light-protected bottles.

Silicon (Czochralski, n-type, (100)-oriented, P-doped) was obtained from either Virginia Semiconductor (Fredericksburg, VA, 1-10 Ω cm resistivity) or Wacker Siltronic (Munich, Germany, 4-8 Ω cm resistivity). Silicon (float zone, n-type, (110)-oriented, Pdoped, 0.7-1.3 Ω cm resistivity) was obtained from the Institute of Electronic Materials Technology (ITME, Warsaw, Poland). The Si-(100) wafers were 500 ± 25 µm thick, polished on one side, and had measured resistivities between 5 and 7 Ω cm. The Si-(110) wafers were 250 ± 25 µm thick, polished on both sides, and had resistivities of 0.8 Ω cm.

36

2.3.2 Fabrication of Macroporous Silicon

Etching of planar Si was performed in an aqueous solution of 5% HF(aq) that contained 10 mM SDS. The etching was performed potentiostatically at 5 V, with vigorous stirring, in a teflon cell equipped with a Pt counter/pseudoreference electrode. Prior to etching, the teflon cell, o-rings, and Pt mesh counter electrode were cleaned in aqua regia (3:1 HCl:HNO₃ by volume) for 30 min. Silicon samples were rinsed sequentially with water, methanol, acetone, methanol, and water, and were then dried under a stream of $N_2(g)$. Approximately 2 cm² of the polished side of the Si was then exposed to the etching solution.

The illumination intensity was adjusted to maintain a constant 10 mA cm⁻² of current during etching, with the light intensity controlled by connecting the lamp power supply to a variable resistor. Samples were etched for 15, 30, 45, or 60 min. The samples were then rinsed thoroughly in water and dried under a stream of $N_2(g)$. To remove the microporous Si layer, the samples were etched in 10% KOH(aq) for 10-20 s, and were then rinsed sequentially with water, methanol, acetone, methanol, and water, followed by drying under a stream of $N_2(g)$.

2.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) data were obtained using a LEO 1550 VP Field Emission SEM (FE SEM) using the in-lens detector at an accelerating voltage of 10 kV. Porous samples were scored on the back and cracked along the (100) directions to obtain cross sectional images, and the resulting pieces were mounted to the SEM stub using carbon tape.

37

2.3.4 Preparation of Photoelectrodes

For photoelectrochemistry, the planar and macroporous silicon samples were scored and cracked to produce $\sim 5 \text{ mm x } 5 \text{ mm}$ electrodes. The samples were then etched for 30 s in buffered HF(aq), rinsed with water, and dried under a stream of $N_2(g)$. Ga/In eutectic was then immediately scratched into the back-side of the samples. Ag paint was then used to affix the back of each sample to a coil of tinned Cu wire. The front surface of the samples was covered with Epoxies, Etc. (Cranston, RI) 20-3004 LV epoxy to leave an exposed area of $\sim 1-2 \text{ mm}^2$. The silicon sample and the Cu wire were then sealed in a glass tube using Hysol 1C epoxy (Loctite, Rocky Hill, CT), with the sample surface oriented perpendicular to the long axis of the glass tube. Most of the LV epoxy was covered with Hysol epoxy. The LV epoxy was needed due to the tendency of the Hysol epoxy to form bubbles on the porous Si surface. Both epoxies are opaque and resistant to methanol, and the Hysol epoxy provided strong structural support. Before use in photoelectrochemical experiments, electrodes were allowed to cure for at least 24 h at room temperature. The projected area of each electrode was measured by taking an image at 800 dpi of the electrodes and a 1 cm x 1 cm calibration square, using a flat-bed scanner, and analyzing the resulting image using the Image SXM software.

2.3.5 Photoelectrochemistry

Photoelectrochemical experiments were conducted in a sealed glass cell under a positive pressure of Ar. The measurement solution (CH₃OH, 1 M LiClO₄, 200 mM Me_2Fc , ~0.1 mM Me_2FcBF_4) was prepared and introduced into the measurement cell under an inert atmosphere. Silicon electrodes were etched (30 s in buffered HF(aq) for

planar samples; 2 min in 1:1 (v:v) 27 M HF(aq):ethanol for porous samples) to remove the native oxide, rinsed with water, and then thoroughly dried under a stream of $N_2(g)$. The electrodes were then immediately introduced into the cell (Figure 2.2), under a positive flow of Ar. The reference electrode was a Luggin capillary, with an outer tip diameter of $\sim 100 \ \mu m$, that contained a Pt wire and a sample of the same solution as in the working electrode compartment. A Pt mesh was used as a counter electrode. The cell had a flat quartz bottom, and the working and



Figure 2.2. Schematic diagram of the photoelectrochemical cell employed. The bottom window of the cell was quartz, and illumination was from a 300 W ELH bulb at 100 mW/cm². The cell contained 200 mM Me₂Fc, ~ 0.1 mM Me₂FcBF₄, and 1.0 M LiClO₄ in anhydrous methanol. The Luggin capillary was filled with the same solution. The cell was stirred vigorously during measurements and kept under positive pressure of Ar.

reference electrodes were positioned as close as possible to the bottom of the cell, with the tip of the Luggin capillary directly underneath the Si surface and as close as possible to the Si without touching its surface. The solution was stirred vigorously during all data collection.

Illumination of the bottom of the cell was provided by a 300 W ELH-type Whalogen bulb equipped with a dichroic rear reflector.⁴³ The illumination intensity was measured using a calibrated Si photodiode that was in turn calibrated relative to a

38

secondary standard Si solar cell. The secondary standard Si solar cell had been calibrated by an independent calibration laboratory with respect to a reference AM 1.0 spectrum at 100 mW cm⁻² of illumination intensity. For Si photoelectrodes in this same cell configuration and electrolyte/redox system, this calibration method has been shown previously to produce short-circuit photocurrent densities that are very close to those obtained under the same intensity of actual sunlight.^{32,37}

All current density-potential (J-E) measurements were recorded using a Solartron model 1287 potentiostat. In a typical experiment, the J-E behavior of the electrode was measured at 10 mV s⁻¹ in the dark, then under \sim 10 mW cm⁻² of illumination, followed by a measurement under 100 mW cm⁻² of illumination, and then measured again in the dark. The open-circuit voltage, V_{oc} , was measured between each J vs E measurement. The short-circuit current density, J_{sc} , was calculated as the average current density for potentials within 10⁻⁴ V of 0 V versus the Nernstian potential of the cell. The values of Voc and the presented J-E behavior are reported with respect to the Nernstian cell potential, which was measured with respect to the reference electrode for each working electrode. The Nernstian potential was typically 10-30 mV vs. the reference electrode potential, due to drift in the composition of the cell solution compared to the composition of the solution in the Luggin capillary. The point of maximum power was calculated as the average of 10 data points, after eliminating the 10 largest measured points (to remove any erroneous spikes). The efficiency and fill factor were calculated by conventional methods. The J-E data shown in the figures were obtained on representative samples, while the values reported in the text and tables for J_{sc} , V_{oc} , fill factors, and energy

conversion efficiencies are the means of values measured on six electrodes for each type (three for (110) samples), with the error reported as the standard error of the mean.

Cyclic voltammograms were collected at various scan rates under the same conditions used for the *J*-*E* data, except that the solution composition was 1.0 M LiClO₄ with 0.3 mM Me₂Fc in CH₃OH, with no Me₂FcBF₄ initially present, and the solution was not stirred. Scans were collected using a Princeton Applied Research Model 173 potentiostat with a Model 175 programmer interfaced to a DAQ card. All experiments were conducted under >100 mW cm⁻² of ELH-type illumination, with identical illumination conditions for all samples. The reported cyclic voltammetric data are the average of the behavior for three electrodes for each sample type, with the error bars representing the standard error of the mean. The diffusion coefficient of Me₂Fc in methanol was calculated from the measured steady-state current at a Pt microelectrode under similar conditions.

2.3.6 Correction for Series Resistance and Concentration Overpotential

Corrections for concentration overpotential and series resistance losses were performed according to equations (2.1) and (2.2):⁴⁴

$$\eta_{conc} = \frac{k_B T}{nq} \left\{ \ln \left(\frac{J_{l,a}}{-J_{l,c}} \right) - \ln \left(\frac{J_{l,a} - J}{J - J_{l,c}} \right) \right\}$$
(2.1)

$$E_{corr} = E_{meas} - iR_s - \eta_{conc} \tag{2.2}$$

where k_B is Boltzmann's constant, T is the absolute temperature, q is the charge on an electron, n is the number of electrons transferred in the redox process (n = 1 for Me₂Fc), $J_{l,c}$ and $J_{l,a}$ are the cathodic and anodic limiting current densities, respectively, and R_s is

the series resistance. The limiting cathodic and anodic current densities were determined as -0.2 mA cm⁻² and 60 mA cm⁻², respectively, by use of a Pt foil working electrode in the same geometry as the Si working electrode, in contact with the same electrolyte solution and in the same cell configuration. The series resistance was calculated by using equation (2.1) to correct the J-E data obtained using the Pt electrode for concentration overpotential losses. The inverse of the slope of the linear portion of the resulting J-Edata, around 0 V vs the cell potential, was then evaluated to produce a value for R_s . Although the series resistance varied from measurement to measurement, due primarily to small differences in the placement of the Luggin capillary, the value was typically in the range of 130-180 Ω . To minimize the possibility of overcorrection, a value of 100 Ω was chosen as the value of the series resistance used in the calculations. This value should be an underestimate of the actual series resistance, particularly because the contact resistance and the series resistance of the silicon are not accounted for by the resistance data obtained using the platinum working electrode. Hence, the photoelectrode efficiencies calculated herein are conservative. Correction of the observed J-E behavior at the Si photoelectrodes for both series resistance and concentration overpotentials thus produced the values of E_{corr} reported herein for each measured potential, E_{meas} .

2.3.7 Analysis of Cyclic Voltammograms

The lithographic-galvanic (LIGA) electrodes analyzed by Neudeck and Dunsch in terms of their cyclic voltammetry behavior are similar to the porous electrodes used in this study.⁴⁵ The LIGA electrodes are hexagonal arrays of pores with regular pore dimensions and pore-pore spacing. The porous electrodes used in this study, although not

regular in pore dimension and spacing, are structurally similar, and therefore their normalized peak current behavior with respect to scan rate can be modeled using the same approach.

Derivation of the expression for the peak potential requires several equations that relate the dimensionless radius, p, to the dimensionless potential, ξ , and the dimensionless current ψ , under various conditions. These quantities can be defined as:

$$p = r \sqrt{\frac{nFv}{RTD}}$$
(2.3)

$$\xi = -\frac{nF}{RT} \left(E - E^0 \right) \tag{2.4}$$

$$\psi = \frac{I}{nFAc\sqrt{nFvD/RT}}$$
(2.5)

where *r* is the radius of the electrode, *n* is the number of moles of electrons involved in the reaction (n = 1 for Me₂Fc), *F* is Faraday's constant, *v* is the scan rate, *R* is the gas constant, *T* is the absolute temperature, *D* is the diffusion coefficient (measured to be 1.02 x 10⁻⁵ cm² s⁻¹ for Me₂Fc in methanol), *E* is the electrode potential, *E*⁰ is the standard potential, *A* is the electrode area, and *I* is the current.

For a tubular electrode, at the peak potential, one obtains:

$$\xi_{tube,p} = 1.11 \frac{\tanh[2.589(\log[p] - 0.4318)] + 1}{2}$$
(2.6)

$$\psi_{tube,p} = 0.446 \frac{\tanh[1.755(\log[p] - 0.2706)] + 1}{2}$$
(2.7)

The dimensionless tubular current at the peak current for a planar electrode is given by:

$$43$$

$$\psi_{tube,1.11} = 0.446 \frac{\tanh[1.999(\log[p] - 0.3285)] + 1}{2}$$
(2.8)

Finally, calculating the dimensionless charge at a tubular electrode at the peak potential for tubular and planar electrodes yields:

$$q_{tube,p} = 0.529 - 0.493 \frac{\tanh[2.271(\log[p] - 0.2706)] + 1}{2}$$
(2.9)

$$q_{tube,1.11} = 0.781 - 0.747 \frac{\tanh[2.063(\log[p] - 0.6965)] + 1}{2}$$
(2.10)

These quantities enable calculation of the peak current at a LIGA-produced macroporous metallic electrode, which will be used to approximate the mass-transportlimited current at a macroporous silicon electrode under high levels of illumination. Defining s_w as the pore width, s_b as the pore-pore spacing, and s_h as the pore length, along with $R_h = s_h/s_w$ and $R_b = s_b/s_w$, produces an expression for the peak potential at a LIGA electrode as:

$$\xi_{LIGA,p}[R_b, R_h, p] = \xi_{tube,p}[p] + \frac{0.446(1.11 - \xi_{tube,p}[p])}{0.446 + \psi_{part}[R_b, R_h, p]}$$
(2.11)

where

$$\psi_{part}[R_{b}, R_{h}, p] = \frac{2R_{h}\psi_{tube, p}[p]}{(1+R_{b})^{2}}$$
(12)

The dimensionless partial current and charge in the pores can then be approximated as follows:

$$\psi_{tube}^{LIGA,p}[R_b, R_h, p] = f_{int}[1.11, \psi_{tube, 1.11}[p], \xi_{tube, p}[p], \psi_{tube, p}[p], \xi_{LIGA, p}[R_b, R_h, p]]$$
(2.13)

$$q_{tube}^{LIGA,p}[R_b,R_h,p] = f_{int}[1.11,q_{tube,1.11}[p],\xi_{tube,p}[p],q_{tube,p}[p],\xi_{LIGA,p}[R_b,R_h,p]]$$
(2.14)

where

$$f_{\text{int}}[x_1, y_1, x_2, y_2, x] = y_1 + \frac{(y_2 - y_1)(x - x_1)}{(x_2 - x)}$$
(2.15)

The dimensionless current at a planar electrode can be approximated by:

$$\psi_{disc} = 0.3801 - 0.1251\xi - 0.0642\xi^2 + 0.00439\xi^3$$
(2.16)

Given these values, the dimensionless peak current at the LIGA electrode can be calculated using:

$$\psi_{LIGA,p}[R_{b},R_{h},p] = \psi_{disc}[\xi_{LIGA,p}[R_{b},R_{h},p]] + (2R_{h}\psi_{tube}^{LIGA,p}[R_{b},R_{h},p] + \psi_{disc}[\xi_{LIGA,p}[R_{b},R_{h},p]] \times (q_{tube}^{LIGA,p}[R_{b},R_{h},p]-1)) \times ((1+R_{b})^{2})^{-1}$$
(2.17)

The peak current is then given by:

$$I_{LIGA,p} = nFA_{disc} c \sqrt{\frac{nFvD}{RT}} \times \psi_{LIGA,p} \left[R_b, R_h, \frac{s_w}{2} \sqrt{\frac{nFv}{RTD}} \right]$$
(2.18)

where A_{disc} is the projected area of the electrode. Equation (2.18) can be rearranged to obtain the desired result in terms of the normalized peak current:

$$J_{p,proj} = \frac{I_{LIGA,p}}{A_{disc}} = nFc \sqrt{\frac{nFvD}{RT}} \times \psi_{LIGA,p} \left[R_b, R_h, \frac{s_w}{2} \sqrt{\frac{nFv}{RTD}} \right]$$
(2.19)

These calculations were performed to fit the peak currents for the porous electrodes normalized by their projected area, $J_{p,proj}$. At each scan rate, the expected peak currents were calculated based on the equations above, and the sum of the squares of the deviations from the measured data was calculated. The value of s_b (which approximates the pore-pore spacing) was then systematically varied to obtain the minimum sum of squares value, while all other parameters were held constant. Each fit always produced a clear minimum in the sum of squares with respect to s_b , typically at $s_b \approx 2 \mu m$, which is consistent with the pore-to-pore spacing observed in the SEM images.

2.4 Results

2.4.1 Morphology of the Macroporous Silicon Samples

Figure 2.3 depicts the macroporous Si samples obtained from the anodic etching process. The pores were \sim 2-3 µm diameter, approximately circular in cross-section, and reasonably uniform over large areas. In addition to fully developed pores, circular etch pits (light gray in Figure 2.3) were observed, which is expected for anodization of n-type



Figure 2.3. Left: Plan view of macroporous silicon etched for 30 min at 10 mA cm⁻². The scale bar is $2 \mu m$. Right: Plan view showing the consistency of the porous surface over a large area. The scale bar is $10 \mu m$.



Figure 2.4. Cross sectional view of macroporous silicon etched for 30 min at 10 mA cm⁻². The scale bar is $10 \,\mu$ m.

silicon under back-side illumination without prior formation of lithographically defined etch pits.¹⁴ Cross-sectional SEM data indicated that the pores were approximately the same length across a given sample, with only minimal branching (Figure 2.4).

Anodization of the samples for 15, 30, 45, and 60 min, respectively, under otherwise nominally identical conditions, produced pores of increasing length. Over the range of times investigated, the pore

length varied linearly with etching time (Figure 2.5), and a maximum pore length of \sim 85 µm was obtained for the times used in this study. However, the pore diameter was nearly independent of etch time.

The time intercept of a fit of pore length vs. time was ~6 min,



Figure 2.5. Plot of pore length vs. etch time. The growth rate was ~1.6 μ m min⁻¹, with a pore initiation time of ~6 min.

which is consistent with a pore initiation phase during the initial etching, followed by uniform pore growth. The illumination intensity required to produce 10 mA cm⁻² of current density dropped rapidly after 6-8 min of etching time, and then dropped much more slowly thereafter. These observations are consistent with a pore initiation phase followed by a steady pore growth phase.

2.4.2 J-E Behavior

Figure 2.6 shows the *J*-*E* behavior of planar (100)- and (110)-oriented n-Si samples, and of macroporous Si electrodes made from (100) n-Si, in contact with the CH₃OH-



Figure 2.6. J-E data at 10 mV s⁻¹ under 100 mW cm⁻² of illumination.

Me₂Fc^{+/0} electrolyte under 100 mW cm⁻² of ELH-type simulated AM 1.5 illumination. The short-circuit photocurrent densities were 5-7 mA cm⁻² lower for the macroporous samples than for the planar (100) sample, but J_{sc} was relatively independent of the pore length.

The open-circuit voltage decreased slightly as the pore length increased, however V_{oc} was still greater than 480 mV even for samples with the longest pores (Table 2.1).

Etch Time	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	Fill Factor (%)	Efficiency (%)
Planar (100)	36.2 ± 2.6	566 ± 2	44.6 ± 1.6	9.1 ± 0.5
15 min	30.6 ± 1.7	552 ± 3	46.0 ± 1.6	7.7 ± 0.3
30 min	29.4 ± 0.9	543 ± 3	44.8 ± 1.9	7.1 ± 0.2
45 min	29.3 ± 1.2	517 ± 8	42.4 ± 1.3	6.4 ± 0.3
60 min	31.5 ± 1.8	485 ± 12	41.3 ± 0.8	6.3 ± 0.5
Planar (110)	31.8 ± 0.8	601 ± 2	46.2 ± 0.9	8.8 ± 0.2

Table 2.1. Figures of merit for raw data

Planar samples exhibited V_{oc} values of 566 mV for the (100)-oriented samples and 600 mV for the (110)-oriented samples. Both of these values are near the bulk recombination/ generation limit for the injection level and the doping level in each sample, which are 573 mV and 612 mV for the (100) and (110) samples, respectively.³⁶ In contrast, macroporous Si samples that had been etched for 60 min from the same stock as the (100)-oriented planar Si samples exhibited $V_{oc} \sim 485$ mV.

Under 100 mW cm⁻² of ELH-type simulated solar illumination, all of the *J-E* data exhibited small limiting cathodic current densities, due to the very small concentration of electron acceptor in the solution (~0.1 mM of Me₂Fc⁺). Photoelectrode energy conversion efficiencies from these data have been shown previously to underestimate the actual energy conversion performance of such systems, due to the appreciable concentration overpotentials and series resistance losses in this cell configuration.^{32,36,46} Consistently, the fill factors of both the planar and porous photoelectrodes increased as the light intensity was lowered to 10 mW cm⁻², in accord with expectations for reduced current-dependent losses in the cell at lower J_{sc} values.

Etch Time	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	Fill Factor (%)	Efficiency (%)
Planar (100)	36.4 ± 2.6	566 ± 2	70.3 ± 1.4	14.4 ± 0.9
15 min	32.6 ± 2.0	552 ± 3	69.1 ± 2.0	12.2 ± 0.7
30 min	30.7 ± 1.2	543 ± 3	68.9 ± 3.1	11.4 ± 0.5
45 min	30.7 ± 1.4	517 ± 8	64.7 ± 1.9	10.2 ± 0.5
60 min	34.0 ± 2.0	485 ± 12	63.9 ± 1.8	10.6 ± 0.8
Planar (110)	32.1 ± 1.1	601 ± 2	73.7 ± 2.9	14.2 ± 0.4

Table 2.2. Figures of merit for corrected data



Figure 2.7. Comparison between raw J-E data and data corrected for series resistance and concentration overpotentials under 100 mW cm⁻² illumination.

Figure 2.7 shows the *J-E* behavior after correction for series resistance and concentration overpotentials.⁴⁴ The planar electrodes had three-electrode (photoelectrode) energy conversion efficiencies of ~14% from incident energy into electrical energy, whereas the macroporous Si samples exhibited photoelectrode efficiencies of 10-12% (Table 2.2).

2.4.3 Cyclic Voltammetry of Planar and Macroporous Si Samples

When the peak current is limited by mass transport of redox species to the electrode surface, as opposed to being under light-limited conditions, the cyclic voltammetric behavior of photoelectrodes probes the morphology of the solid/liquid contact and provides a measure of the junction area accessible to photogenerated minority carriers. Cyclic voltammetric data as a function of scan rate were thus collected to evaluate the photoactive junction area for the macroporous Si electrodes relative to those of the planar Si electrodes.

The planar Si(100) samples showed the expected linear relationship between the cyclic voltammetric peak anodic current density and the square root of the scan rate (Figure 2.8). In solutions similar to those used for the cyclic voltammetry experiments, the diffusion coefficient of Me_2Fc in

methanol was measured at a Pt microelectrode to be 1.02 x 10⁻⁵ cm² s⁻¹. The planar Si samples thus generally exhibited slightly smaller peak currents than expected based on the concentration of Me₂Fc used and the measured diffusion coefficient of Me₂Fc in methanol, but behaved in general in accord with expectations.

The peak current data measured



Figure 2.8. Peak current density versus square root of the scan rate for planar (100)-oriented Si samples in methanol with 0.3 mM Me₂Fc and 1.0 M LiClO₄. The dashed line indicates the calculated peak current density for these samples based on the measured electrode area and diffusion coefficient of Me₂Fc, and is not a fit to the data. Error bars represent the standard error of the mean.

from the cyclic voltammetric behavior of macroporous Si electrodes, normalized to the projected area of the electrodes, are displayed in Figure 2.9. At fast scan rates, v, all of the porous electrode samples showed significantly higher projected-area-normalized peak current densities, $J_{p,proj}(v)$, than the mass-transport-limited current densities measured at, or expected theoretically for, planar Si electrodes. At any given high scan rate, $J_{p,proj}(v)$



Figure 2.9. Peak current density normalized to the projected area versus square root of the scan rate for macroporous Si electrodes produced by etching (100)-oriented Si samples for a) 15 min, b) 30 min, c) 45 min, and d) 60 min. The data were obtained in methanol with 0.3 mM Me₂Fc and 1.0 M LiClO₄. The solid lines indicate the fit to the data using the model of Neudeck and Dunsch and allowing the pore-pore spacing as the only adjustable parameter.⁴⁵ The dashed line indicates the calculated peak current density for these samples based on the measured electrode area and diffusion coefficient of Me₂Fc assuming a planar electrode, and are not a fit to the data. Error bars are the standard error of the mean.

consistently increased with increasing pore length, as produced by an increase in etching time and as measured by SEM data. The pore morphology was largely unchanged with increasing etch time, while the pore length increased linearly, so the surface area and thus the values of $J_{p,proj}(v)$ are expected to increase with etching time, in accord with observations.

51

The normalized peak current data for the macroporous Si photoelectrodes were fitted using a theory that has been developed previously for the voltammetric behavior of microstructured metal electrodes that have a geometry very similar to that of the macroporous Si electrodes described herein.⁴⁵ The pore-pore spacing was allowed to vary while the pore diameter and pore length were fixed to the values measured from SEM images. The fit typically yielded values of the pore-pore spacing on the order of 2 μ m, which is consistent with the SEM images of the porous samples. The analysis of the cyclic voltammetric data is thus consistent with a model in which photogenerated minority carriers can access the entire surface area of the solid/liquid junction on the macroporous Si photoelectrode samples studied herein.

2.5 Discussion

The *J-E* data under simulated AM 1.5 illumination suggest that the macroporous Si electrodes, despite their rough surface and high surface area, can provide high solar energy conversion efficiencies. The open-circuit voltage remained relatively large despite the increase in surface area by a factor of at least 15 for the macroporous samples relative to the planar samples, based on estimates from SEM images. Although these porous silicon samples were made from single crystalline silicon, they demonstrate that it is possible, in a geometry with a high surface area and an irregular surface, to retain good collection of charge carriers without significant surface-based recombination losses. Hence, it ought to be possible to use low diffusion length materials in efficient solar energy conversion devices, provided that the directions of charge-carrier generation and collection can be separated.

The $V_{\rm oc}$ values did, however, decrease measurably with increasing pore length. Specifically, planar (100)-oriented Si samples exhibited $V_{oc} \sim 566$ mV, while the macroporous Si samples with the longest pores exhibited $V_{oc} \sim 485$ mV under the same conditions. A fundamental factor that contributes to this decrease is that V_{oc} is expected to be smaller at electrodes that have a high junction area per unit of projected area, because a constant excitation carrier flux from a fixed intensity light source will produce a lower flux of photogenerated charge carriers through the larger accessible junction area. The cyclic voltammetry data clearly indicate that the junction area is electrically active and that minority carriers are capable of being transferred across the entire exposed surface area of all of the macroporous Si samples investigated herein. The steady-state charge-carrier concentrations at the junction set the positions of the quasi-Fermi levels, which in turn determine V_{oc} . A lower minority-carrier flux will thus produce a lower quasi-Fermi level splitting, and therefore a lower value of Voc, at systems having a high junction area per unit of projected area.^{39,47,48} The V_{oc} of 566 mV observed for the planar Si(100) electrode is close to the bulk recombination/generation limit for such samples. If the flux of photogenerated carriers is instead distributed uniformly over a much larger junction area, the bulk recombination/generation limit on V_{oc} will be reduced, as given by the diode equation:

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}}{\gamma J_0} \right)$$
(2.20)

where J_0 is the saturation current density, J_{sc} is the short-circuit current per unit of projected device area, and γ is the actual junction area per unit of projected area of the

device. For the limit of a uniform minority carrier flux with $\gamma = 15$, characteristic of the macroporous Si samples with the longest pores studied herein, equation (2.20) implies that $V_{\rm oc}$ will be reduced by ~70 mV relative to the situation with $\gamma = 1$, in accord with the observed decrease from 566 mV to ~485 mV between the planar and macroporous Si samples investigated herein. The estimated value of γ assumes smooth pore sidewalls with no branching, and is therefore a lower limit on the actual junction area per unit of projected area. Surface recombination may also contribute somewhat to the observed decrease in Voc, because increasing the junction area would also result in an increased rate of surface-derived recombination for the macroporous Si samples, which have a higher solid/liquid junction area per unit of projected area than a planar device. However, surface recombination at n-Si surfaces in contact with CH₃OH-Me₂Fc^{+/0} is very low, on the order of 20 cm s^{-1,16} The porous surfaces contain exposed off-angle planes, but measurements of V_{oc} for (110)-oriented Si samples, performed herein, also yielded bulk recombination-limited photovoltages for the planar, (110)-oriented, n-Si surfaces. Hence, surface recombination is expected to provide a relatively small contributon to the 80 mV decrease in V_{oc} observed for the macroporous Si samples having the longest pores. A precise assessment of the exact value of the theoretically expected reduction in V_{oc} in the system of interest under white light excitation will require a detailed 2-dimensional description of the carrier generation and transport profiles in the macroporous Si samples of concern.

The decrease in V_{oc} with increasing junction area represents a fundamental limitation on micro- and nano-structured semiconductor devices for solar energy

conversion, and should be carefully considered in any new design scheme involving either nanoparticles, nanorods, interpenetrating networks, or other systems having a high junction area per unit of projected device area. This factor highlights the importance of selecting a device geometry that has short path lengths for minority carrier collection, while insuring that the microscopic junction area is as small as possible. Regardless, the high efficiencies observed in this study establish that it is indeed possible to efficiently convert light energy into electrical energy using highly structured materials.

2.6 References

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