# Microwave Reflectance Studies of Photoelectrochemical Kinetics at Semiconductor Electrodes. 2. Hydrogen Evolution at p-Si in Ammonium Fluoride Solution

Michael J. Cass,<sup>†</sup> Noel W. Duffy,<sup>‡</sup> Laurence M. Peter,<sup>\*,‡</sup> Stephen R. Pennock,<sup>§</sup> Shin Ushiroda,<sup>‡</sup> and Alison B. Walker<sup>†</sup>

Department of Physics, Department of Chemistry, and Department of Electrical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

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Microwave reflectance methods have been used to study the kinetics of photogeneration of hydrogen on p-Si in acidic fluoride solutions. To estimate the rate constant for interfacial electron transfer, the magnitude of the observed steady-state light-induced microwave reflectivity change has been compared quantitatively with theoretical predictions based on numerical calculation of the electron and hole profiles in the silicon sample. In addition, the transient and periodic microwave reflectivity responses to stepped and sinusoidally modulated illumination, respectively, have been analyzed to obtain information about the electrode kinetics. The time constants for relaxation of the light-induced conductivity derived from this analysis confirm that electron transfer during hydrogen evolution is slow. The apparent inconsistency in the values of the phenomenological electron-transfer rate constants derived from the steady-state and transient or periodic responses can be resolved if it is assumed that hydrogen evolution proceeds via electron capture by protons followed by a slow bimolecular step leading to molecular hydrogen. Surface charging as the result of slow kinetics is expected to lead to band edge unpinning even at low light intensities, and the existence of this effect has been confirmed by transient photocapacitance measurements.

## Introduction

The mechanism and kinetics of the electrochemical hydrogen evolution reaction (HER) at metal electrodes have been studied extensively. Both the mechanism and the rate of the electrode process depend strongly on the nature of the metal, since the reaction involves an adsorbed hydrogen intermediate. Although generation of hydrogen at illuminated semiconductor electrodes has attracted attention as a possible route for the production of hydrogen from solar energy,<sup>1,2</sup> surprisingly little is known about the mechanism and kinetics of the process. Illumination of p-type semiconductors leads to the generation of excess electrons that can, in principle, reduce protons to hydrogen in a two-step reaction, provided that the energy of the conduction band lies above the hydrogen redox level. In practice, modification of the semiconductor surface by deposition of an electrocatalyst such as platinum is often used to enhance the efficiency of the process.<sup>3,4</sup> It is known that the photogenerated hydrogen may modify the properties of the semiconductor photocathode, introducing near surface recombination centers, as in the case of p-GaP,<sup>5</sup> or a disordered compensated layer, in the case of silicon.6-8

In the present study, photoelectrochemical hydrogen evolution on oxide free Si(111) surfaces has been studied by light-induced microwave reflectivity methods. The results offer new insights into the kinetics and mechanisms of the hydrogen evolution reaction and illustrate the potential of the experimental approach for wider application.

## Theory

The theory of light-induced microwave reflectance changes at the semiconductor electrolyte junction was developed initially by Kunst and Tributsch, together with their collaborators.<sup>9-15</sup> In a preceding paper in this series,<sup>16</sup> we have reviewed the theoretical foundations for the interpretation of light-induced microwave reflectivity measurements, including the responses to transient and periodic illumination. Profiles of the electron and hole concentrations computed numerically from a Hall Shockley Read model of the semiconductor|electrolyte junction were used to calculate the mean change in electronic conductivity,  $\langle \Delta \sigma \rangle$ , of the silicon sample as a function of photon flux, band bending, and rate constant for interfacial electron transfer. The corresponding normalized microwave reflectivity change,  $\Delta R_{\rm M}$ , was calculated by solving the Fresnel equations for a multilayer model to represent the calculated electron and hole profiles. Comparison of the results of the conductivity and reflectivity calculations confirmed that, to a good approximation, the microwave reflectivity change  $\Delta R_{\rm M}$  can be related linearly to  $\langle \Delta \sigma \rangle$ , as proposed by Kunst and Tributsch:

$$\Delta R_{\rm M} = \frac{\Delta P_{\rm r}}{P_{\rm i}} = R_{\rm M} \frac{\Delta P_{\rm r}}{P_{\rm r}} = S \langle \Delta \sigma \rangle = \frac{Sq}{d} \int_0^d [\mu_n \Delta n(x) + \mu_p \Delta p(x)] \, \mathrm{d}x \quad (1)$$

Here  $P_i$  and  $P_r$  are the incident and reflected microwave power, respectively,  $\Delta P_r$  is the change in reflected microwave power,  $R_M$  is the unperturbed microwave reflectivity, *S* is a sensitivity factor, *d* is the sample thickness, *q* is the elementary charge,  $\Delta n(x)$  and  $\Delta p(x)$  are the position dependent excess electron and hole densities resulting from illumination, and  $\mu_n$  and  $\mu_p$  are the electron and hole mobilities.

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<sup>\*</sup> Corresponding author. E-mail: 1.m.peter@bath.ac.uk.

<sup>&</sup>lt;sup>†</sup> Department of Physics.

<sup>&</sup>lt;sup>‡</sup> Department of Chemistry.

<sup>§</sup> Department of Electrical Engineering.

The interpretation of time and frequency resolved microwave reflectance measurements was also reviewed in the first paper.<sup>16</sup> Here it was shown that the time constant for the response to step and sinusoidal illumination profiles is given by

$$\tau = (k_1 + k_{\rm rec})^{-1} \tag{2}$$

where  $k_1$  and  $k_{rec}$  are first-order rate constants (s<sup>-1</sup>) for electron transfer and electron—hole recombination, respectively. These first-order rate constants arise from a phenomenological formulation of kinetics in terms of the nominal surface concentrations of electrons and holes.<sup>17</sup> In order of magnitude terms at least,  $k_1$  (s<sup>-1</sup>) can be related to  $k_2$  (cm<sup>4</sup> s<sup>-1</sup>), the second-order heterogeneous rate constant for interfacial electron transfer, and to  $k_{tr}$  (cm s<sup>-1</sup>), the pseudo-first-order heterogeneous rate constant for electron transfer (obtained by assuming a constant concentration of redox species in the interfacial region):

$$k_1 = \frac{k_{\rm tr}}{\delta} = \frac{k_2 N_{\rm redox}}{\delta} = v_{\rm th} \sigma_{\rm redox} N_{\rm redox}$$
(3)

Here  $\delta$  is a nominal reaction layer thickness or tunneling length for electron transfer at the interface,  $v_{\text{th}}$  is the thermal velocity of minority carriers, and  $\sigma_{\text{redox}}$  is the capture cross section for the reaction of minority carriers with redox species present with a volume density of  $N_{\text{redox}}$  in the solution.<sup>18</sup>

Royea et al.<sup>19</sup> have estimated an upper limit for the rate constant  $k_2$  for outer sphere reactions at semiconductor electrodes in the range  $(1-10) \times 10^{-17}$  cm<sup>4</sup> s<sup>-1</sup>. If we assume a concentration of redox species equal to  $10^{-2}$  M, for example, the upper limit of  $k_{tr}$  is in the range 60-600 cm s<sup>-1</sup>, and the corresponding range for  $k_1$  is  $6 \times 10^8$  to  $6 \times 10^9$  s<sup>-1</sup>. In practice, such rapid electron transfer will effectively prevent the buildup of minority carriers at the interface, and as shown in the preceding paper,<sup>16</sup> the light-induced microwave response will be too small to measure.

For quantitative interpretation of the steady-state microwave reflectivity response, it is necessary to determine the sensitivity factor, *S* (cf. eq 1). This can be done using potential-modulated microwave reflectance (PMMR).<sup>20,21</sup> The mean conductivity of a semiconductor electrode under depletion conditions can be perturbed in the dark by changing the potential. Since the density of electrons and holes in the depletion region can be neglected, eq 1 can be simplified to

$$\Delta R_{\rm M} = S \langle \Delta \sigma \rangle = \frac{Sq}{d} \mu_p p_0 \Delta W_{\rm sc} = \frac{S}{d} \mu_p \Delta Q_{\rm sc} = \frac{S}{d} \mu_p C_{\rm sc} \Delta V \quad (4)$$

Here  $\Delta W_{\rm sc}$  is the change in the width of the space charge region,  $p_0$  is the bulk hole concentration,  $\Delta Q_{\rm sc}$  is the change in the space charge,  $C_{\rm sc}$  is the space charge capacitance, and  $\Delta V$  is the amplitude of the ac potential modulation. The linear relationship between the microwave and capacitance responses implied by eq 4 allows the sensitivity factor, *S*, to be determined experimentally and compared with theoretical calculations based on the Fresnel equations for a four-layer model: air|bulk Si|depleted Si|solution.

Figure 1 shows the potential modulated microwave response calculated from the four-layer model for 100 mV rms modulation and band bending of 1.2 eV (similar calculations for the lower frequency X-band 10 GHz system have been reported by Searson et al.<sup>22</sup>). The doping density used in the calculation was  $10^{15}$  cm<sup>-3</sup>. The unperturbed reflectivity of the silicon sample is 0.50, and  $\Delta R_{\rm M}$  (peak to peak) is  $8.5 \times 10^{-6}$ . The sensitivity factor calculated from  $\Delta R_{\rm M}$  using eq 4 is 0.27  $\Omega$  cm.



**Figure 1.** Continuous line: potential modulated microwave reflectivity calculated from the Fresnel equations using a four-layer model, air|bulk Si|depleted Si|electrolyte. The broken line shows the ac potential modulation. Wafer thickness = 350  $\mu$ m; acceptor density = 10<sup>15</sup> cm<sup>-3</sup>. Band bending = 1.2 eV. Calculated dc reflectivity,  $R_M(0) = 0.50$ .  $\epsilon_{si} = 12.0$ .  $\epsilon_{electrolyte} = 20$ ;  $\sigma_{electrolyte} = 10^{-6} \Omega^{-1}$  cm<sup>-1</sup> (this low value of the conductivity was chosen to eliminate interference effects and to represent the open waveguide configuration).

## **Experimental Section**

Measurements were performed with a Ka-band microwave system. The microwave source was a Gunn diode (33 GHz, Atlantic Microwave limited) mounted on a rectangular Ka-band waveguide (7 mm  $\times$  3 mm). The silicon wafer was mounted on the end of the waveguide in the base of a PTFE flow cell (see below). The reflected microwave power was measured using a crystal detector (R422C, Agilent technology) via a directional coupler (Flann Microwave). An isolator ensured that the microwave field was not reflected back to the microwave source, and a variable attenuator allowed adjustment of the power of the microwave field. Addition of a second directional coupler allowed measurement of  $R_{\rm M}$ , the absolute microwave reflectivity of the sample.

Boron doped p-Si(111) samples (ITME, 8–12  $\Omega$  cm) were used in the measurements. The acceptor doping density obtained by analysis of Mott Schottky plots was 7 × 10<sup>14</sup> cm<sup>-3</sup>. Cut samples were etched for 30 s in flowing CP-4A solution (3:5:3 by volume 48% HF:concentrated HNO<sub>3</sub>:100% CH<sub>3</sub>COOH) and rinsed with Milli-Q water. This procedure removed about 20  $\mu$ m from the front surface of the wafers, eliminating the polishing damage created during wafer manufacture that was found to enhance hydrogen uptake. Ohmic contact was made around the periphery of the wafer using the Ga|In eutectic. The ohmic losses in this configuration are negligible due to the small size of the Ka-band waveguide (7 mm × 3 mm).

The 1 M fluoride (pH 3) solution contained 0.5 M  $NH_4F$  (40%, BDH, Aristar), 0.15 M  $NH_4Cl$  (Aldrich, ACS reagent), and 0.5 M HF (48%, BDH, AnalaR). The electrolyte was degassed with nitrogen for 10 min before starting experiments and was circulated continuously through the flow cell via a gravity-fed reservoir with a nitrogen lift pump.

Measurements were made in a three-electrode PTFE flow cell equipped with Pt wire counter and Ag/AgCl reference electrodes. The cell was machined to fit the end of the Ka waveguide, and the silicon sample was mounted in its base so as to expose an area of 0.21 cm<sup>2</sup> to the electrolyte. Kapton tape was used to isolate the silicon from the waveguide. The working electrode potential was controlled by a low-noise potentiostat programmed by the analog output of a computer-controlled Stanford Research SR830 lock-in amplifier. Steady-state capacitance and PMMR measurements were made using a frequency of 270 Hz. Transient photocapacitance measurements were made at a frequency of 10 kHz. Intensity-modulated photocurrent spectroscopy (IMPS) and light-modulated microwave reflectance (LMMR) measurements were performed by illuminating the sample with a red light emitting diode (LED:  $\lambda = 626$  nm). Sinusoidal intensity modulation of the LED output was achieved by using a current driver programmed by the lock-in amplifier. The current and microwave responses were detected simultaneously by two synchronized lock-in amplifiers (Stanford Research SR830). A Stanford Research SR560 low-noise preamplifier was used to amplify the signal from the microwave detector. The illumination intensity was controlled using a set of calibrated Schott neutral density (NG) filters. Light intensities were measured with a calibrated silicon diode. The frequency dependent lightmodulated microwave and photocurrent responses were fitted using a nonlinear least-squares program (Solartron Z-View).

For the time resolved microwave and photocurrent measurements, the LED driver was programmed by a square pulse generator to give a 2 s on period followed by a 12 s off period. The microwave detector was connected to one channel of a Stanford SR560 low noise differential preamplifier, and the other channel was used to offset the dc microwave signal to zero using a Zener-stabilized dc source. The offset output was then averaged using a digital oscilloscope (Tektronix TDS3012). A typical experiment involved accumulation and averaging of 160 samples. Transient photocapacitance measurements were made using a Stanford lock-in amplifier at a modulation frequency of 10 kHz. The rise and decay of the microwave and capacitance signals were fitted using nonlinear fitting routines in SigmaPlot.

#### **Results and Discussion**

**Experimental Determination of the Sensitivity Factor.** The sensitivity factor relating the microwave response to the change in mean conductivity (cf. eq 1) was determined by measuring the potential-modulated microwave response of the p-Si|NH<sub>4</sub>F system in the dark. In this case, potential modulation under depletion conditions changes the width of the space charge region, and the modulated microwave reflectivity is linearly related to the space charge capacitance, which can be measured at the same time (cf. eq 4). This relationship is illustrated by Figure 2a, which compares the potential dependence of the microwave and capacitance responses for a freshly etched p-Si(111) sample in ammonium fluoride (pH 3.0).

 $R_{\rm M}$ , the unperturbed reflectivity of the silicon sample, was found to be 0.6, which is 20% higher than the value calculated from the four-layer model. The experimental sensitivity factor determined from Figure 2a is 0.53  $\Omega$  cm, which is twice the value calculated using the four-layer Fresnel model. The reason for these differences is not clear, but it may arise from simplifications made in the four-layer Fresnel calculation.

The linear relationship between  $\Delta R_{\rm M}$  and  $C_{\rm sc}$  allows the PMMR data to be used to construct a Mott Schottky plot,<sup>20,23</sup> as shown in Figure 2b. The plot shown here was constructed from data obtained for a fresh sample. The flatband potential was found to move progressively to more positive potentials following prolonged illumination of the electrode. This effect has been reported elsewhere<sup>7,24</sup> and attributed to the effect of incorporation of photogenerated hydrogen into the near-surface region of the silicon. Fresh samples and low light intensities were used in the present work in order to minimize the effects of hydrogen incorporation as far as possible.

**"Steady-State"** Microwave Response under Illumination. The photocurrent and microwave responses of p-Si(111) were characterized as a function of potential and light intensity. For these measurements, the light was modulated at a low frequency



**Figure 2.** (a) Comparison of the potential dependence of the capacitance and PMMR responses of p-Si(111) in 1.0 M ammonium fluoride solution (pH 3). Modulation frequency = 270 Hz. Modulation amplitude = 100 mV rms. (b) Microwave Mott Schottky plot constructed from the  $\Delta R_{\rm M}$  data for a freshly etched silicon sample.



**Figure 3.** Set of photocurrent voltage curves for p-Si(111) in 1.0 M ammonium fluoride solution (pH 3). The plots have been normalized to the incident photon flux. Modulation frequency = 10 Hz. Values of the saturation photocurrent density (in  $\mu$ A cm<sup>-2</sup>): (1) -0.7; (2) -7.6; (3) -91. The photocurrent calculated from the Gärtner equation is also shown (4). Note the displacement of the photocurrent onset potential away from the flatband potential with increasing light intensity.

(10 Hz). The normalized photocurrent voltage plots in Figure 3 illustrate the characteristic displacement of the photocurrent onset potential that is observed as the illumination intensity is increased. Possible reasons for this effect include surface charging and enhanced surface recombination via photogenerated intermediates (in this case hydrogen atoms).



**Figure 4.** (a) Set of "steady state"  $\Delta R_{\rm M}$  plots for different illumination intensities. The values of the saturation current densities are the same as those shown in Figure 3. Note that the plots are not normalized with respect to the incident photon flux. (b) Plot showing the nonlinear intensity dependence of the light-induced microwave reflectivity. The limiting linear slope shown by the broken line was used to estimate  $k_{\rm tr}$  from the steady-state response.

The corresponding microwave–voltage plots shown in Figure 4a have not been normalized, since, as Figure 4b shows,  $\Delta R_{\rm M}$  varies nonlinearly with the saturation photocurrent. This non-linearity could indicate that the mobility of electrons in the near surface region is not constant but falls as the electron density increases. This behavior had been noted for accumulation and inversion layers.<sup>25–27</sup> However, as shown below, it is more likely that the nonlinearity arises predominantly from the kinetics and mechanism of the two-step hydrogen evolution reaction, which give rise to an intensity dependence of  $k_1$ .

In principle, the magnitude of the microwave response can be used to estimate the electron-transfer rate constant. A calculation of  $\Delta R_{\rm M}$  as a function of  $k_{\rm tr}$  for parameter values (doping density, band bending, light intensity, wavelength) corresponding to those used in the present experiments is shown in Figure 5 in the first paper in this series.<sup>16</sup> In view of the nonlinearity of the experimental response as a function of illumination intensity, the linear response seen at low photon fluxes (cf. Figure 4b) was used to estimate the value of  $k_{tr}$  of around 5  $\times$  10^{-4} cm s^{-1}. If we assume a tunneling distance  $\delta$ of the order of 1 nm, this value of  $k_{tr}$  should correspond to a  $k_1$ value of 5  $\times$  10<sup>3</sup> s<sup>-1</sup>. However, as shown below, the time and frequency resolved responses of the system suggest a substantially smaller value of  $k_1$  of 20–30 s<sup>-1</sup>. It should be noted here that the calculation of  $\Delta R_{\rm M}$  as a function of  $k_{\rm tr}$  was made using the electron mobility for bulk silicon. If the electron mobility in the near surface region is lowered by processes such as



**Figure 5.** (a) Comparison of the transient photocurrent (lower trace) and microwave (upper trace) responses of p-Si(111) in 1.0 M ammonium fluoride solution (pH 3). Potential = -1.0 V vs Ag|AgCl. Compare the square photocurrent response typical of the saturation region with the much slower rise and fall of the microwave response. (b) Light-induced microwave response under the same conditions as those for part a, showing the slow decay component of the decay following an illumination pulse.

surface scattering,  $\Delta R_{\rm M}$  will be smaller, but this effect is not be large enough to explain the difference of more than 2 orders of magnitude between the  $k_{\rm tr}$  values derived from the steady-state and time/frequency resolved measurements (see below).

**Time Resolved Microwave and Photocurrent Responses.** Figure 5a contrasts the photocurrent and microwave responses to a step light function in the photocurrent saturation region. The photocurrent follows the illumination essentially instantaneously, since recombination is negligible. By contrast, the rise and fall of the microwave response are much slower. Figure 5b shows that there are two components in the decay of the microwave signal when the light is switched off. Since the recovery of the microwave signal is very slow in the dark, a 1 to 10 light/dark duty cycle was used in the measurements, which were restricted to low light intensities  $(3.5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1})$  to minimize buildup of hydrogen in the silicon.

The rise of the microwave response was fitted to a single exponential, whereas the decay was fitted to a double exponential to take into account the very slow relaxation process that can be seen in Figure 5b. Figure 6a shows an example of the satisfactory nonlinear least-squares fit to a single exponential obtained for the rising part of the microwave transient. Since recombination is negligible at the potential of the measurement, the time constant is equal to the inverse of the rate constant  $k_1$ , which was found to be 28 s<sup>-1</sup>. An identical value of  $k_1$  was obtained for the faster component of the microwave reflectivity decay. The time constant of the slow decay was found to be 0.5 s. It is not clear what causes the slow decay of the microwave reflectivity in the dark, but we attribute it tentatively to a change in the dielectric constant of the sample due to the incorporation



**Figure 6.** (a) Expanded plot of  $\Delta R_{\rm M}$  data from Figure 5a, showing the nonlinear least-squares fit of the rising part to a single time constant. (b) Photocurrent and microwave responses at -0.35 V vs Ag|AgCl. Note the decay of the photocurrent (lower trace) associated with electron-hole recombination. The microwave response has been fitted to a single exponential corresponding to a time constant corresponding to  $(k_1 + k_{\rm rec}) = 55 \text{ s}^{-1}$ .

of subsurface hydrogen. The possibility that it is due to band edge unpinning was excluded by the results of transient photocapacitance measurements (see below).

In the onset region of the photocurrent-voltage curve, the transient photocurrent response exhibits the decay and overshoot characteristic of the competition between recombination and interfacial charge transfer.<sup>28</sup> The microwave response, by contrast, still rises and falls exponentially. The time constant in this case is determined by the sum  $k_1 + k_{tr}$ , rather than  $k_{tr}$  as is the case in the photocurrent saturation region. These differences are illustrated by Figure 6b, which compares the photocurrent and microwave responses observed at a potential of -0.35 V vs Ag|AgCl when the light is switched on. In this case, the rise and fall of the microwave were found to correspond to  $(k_1 + k_{rec}) = 55$  s<sup>-1</sup>.

**Frequency Resolved Microwave and Photocurrent Responses.** In a previous study we showed that light-modulated microwave reflectivity measurements could be used to obtain  $k_1$  and  $k_{rec}$ .<sup>29</sup> A typical set of LMMR plots obtained at low light intensity is presented in Figure 7a. The plots have been normalized to the limiting response measured in the photocurrent saturation region where recombination is negligible. The plots illustrate clearly the effect of band bending. In general, the radial frequency at which the minimum in the semicircular plots occurs is equal to ( $k_1 + k_{rec}$ ). In the photocurrent saturation region, the radial frequency is equal to  $k_1$ , since recombination is negligible.

IMPS can be used in the photocurrent onset region to obtain  $k_1$  and  $k_{tr}$ . Figure 7b shows a set of normalized IMPS plots obtained at the light intensity used in the LMMR experiments. In the case of IMPS, the largest semicircle is seen at the start



**Figure 7.** (a) Set of normalized LMMR plots showing the increase in diameter of the semicircles with increasing band bending, tending toward the limiting response in the photocurrent saturation region, where electron-hole recombination is negligible. The arrow shows the direction of increasing modulation frequency (range 0.45–4.5 kHz, 5 steps per decade). The value of the sum  $(k_1 + k_{tr})$  is obtained from the radial frequency at which the minimum of the semicircle occurs. In the photocurrent saturation region, the radial frequency of the minimum is equal to  $k_1$ . Saturation dc photocurrent =  $-3.6 \ \mu A \ cm^{-2}$ . (b) Corresponding set of normalized IMPS plots showing the decrease in diameter of the semicircles with increasing band bending, tending toward the limit of a point in the saturation current region. The sum  $(k_1 + k_{tr})$  is obtained from the radial frequency at which the maximum of the semicircle occurs, but by contrast with part a, no analysis is possible in the photocurrent saturation limit.



**Figure 8.** Values of  $k_1$  and  $k_{rec}$  derived from the LMMR and IMPS for the same conditions as those for Figure 7. Note that  $k_1$  is only weakly potential dependent, whereas  $k_{rec}$  decreases with increasing band bending. The slope of the fitted line is 180 mV per decade.

of the photocurrent onset region, whereas the response in the saturation region contracts to a point at unity on the real axis and all information about electron-transfer kinetics is lost. The low-frequency intercepts and the angular frequencies at which the maxima in the semicircles occur were used to obtain values of  $k_{tr}$  and  $k_1$ , and good agreement was found with the values obtained by LMMR.

Figure 8 shows that the values of  $k_1$  derived by analyzing the low-intensity LMMR and IMPS data vary little with potential.  $k_{rec}$ , on the other hand, varies with potential, since the recombination rate depends on the surface hole concentration. In the simplest case where no band edge unpinning occurs as the result of surface charging, the slope of the semilogarithmic



**Figure 9.** Double logarithmic plot showing that  $k_1$  and the dc microwave reflectivity response appear to depend on the square root of the incident photon flux (the *x* axis corresponds to the magnitude of the saturation photocurrent density). Both sets of data were derived by analysis of the LMMR response.

plot should be 59 mV per decade, corresponding to the Boltzmann equation describing the surface hole density in the nondegenerate case. However, the experimental value of the slope is 180 mV per decade, indicating a much weaker potential dependence of the recombination rate. As shown below, significant band edge unpinning occurs as the result of surface charging, even at the very low light intensities used in this study. Surface charging is a consequence of the very low rate constant for electron transfer, and it leads to a less rapid variation of surface hole density with applied potential than is the case for an ideal junction.

LMMR measurements made over a range of intensities revealed that the rate constant for interfacial electron transfer increases with intensity, as shown in Figure 9. The results suggest that  $k_1$  varies with the square root of intensity. Since (in the absence of surface recombination) the electron concentration at the surface is a linear function of  $k_1$  and of light intensity, one would expect a square root dependence of  $k_1$  to result in a square root intensity dependence of the steady-state microwave response. The steady-state microwave response can be derived from the low-frequency intercept of the LMMR plots on the real axis. Figure 9 confirms that the low-frequency limit of the microwave response also appears to follow the same square root intensity dependence. This is not expected for a simple one-electron-transfer process, but of course, the hydrogen evolution reaction is a two-step process.

At the simplest level of analysis, two mechanisms can be considered, depending on whether the hydrogen atom intermediate,  $H^{\circ}$ , is mobile or not:

$$H^+ + e \to H^0 \tag{5a}$$

Followed by either (H<sup>0</sup> not mobile)

$$H^+ + H^0 + e \rightarrow H_2 \tag{5b}$$

or (H<sup>0</sup> mobile)

$$H^0 + H^0 \to H_2 \tag{5c}$$

We have analyzed the IMPS response for analogous twostep mechanisms previously in considerable detail for the case in which the steps are irreversible.<sup>17</sup> If recombination is negligible, it can be shown that the apparent or phenomenological rate constant for the mechanism involving eq 5a followed by eq 5c is given by

$$k_1 = \frac{k_a (8k_c g)^{1/2}}{k_a + (8k_c g)^{1/2}}$$
(6a)

Here  $k_a$  and  $k_c$  are the rate constants for steps 5a and 5c, respectively, and g is the flux of electrons into the surface given by the Gärtner equation. In the limit that  $k_a$  is much greater than  $(8k_cg)^{1/2}$ , eq 6a simplifies to a square root dependence of the phenomenological rate constant on light intensity given by

$$k_1 = (8k_4g)^{1/2} \tag{6b}$$

and the steady-state surface concentration of the  $\mathrm{H}^{0}$  intermediate is given by

$$[\mathrm{H}^{0}] = \left[\frac{g}{k_{4}}\right]^{1/2} \tag{6c}$$

The surface concentration of electrons is given by

$$n_{\rm surf} = \frac{g}{k_{\rm a}} \tag{6d}$$

However, if the first step (electron capture by protons) is not only fast but also reversible, the electron concentration will also depend on the square root of the illumination intensity. It therefore appears possible to explain the observed intensity dependence of the phenomenological rate constant by the mechanism outlined above.

The value of  $k_4$  derived from eq 6b is  $6 \times 10^{-12}$  cm<sup>2</sup> s<sup>-1</sup>, and the surface coverage with H<sup>0</sup> derived from eq 6c is about  $10^{12}$  cm<sup>-2</sup> at a current density of 3  $\mu$ A cm<sup>-2</sup>. The corresponding surface electron density can be much lower, since it depends on the forward and reverse rate constants of the first step involving electron capture (and release) by protons and not on the phenomenological rate constant that determines the LMMR and IMPS responses. However, further work will be required to establish the details of the mechanism unequivocally.

**Transient Photocapacitance Measurements.** The buildup of H<sup>0</sup> (and of electrons) at the surface will lead to surface charging. In the case of H<sup>0</sup>, the charging arises from the capture of an electron by a proton. We speculate that protons may be located in the near-surface region in the same way as has been observed for p-GaP in our previous work.<sup>30</sup> The mechanistic analysis in the preceding section suggests that the surface concentration of H<sup>0</sup> is greater than that of electrons, as a consequence of step 5a. The surface (or near-surface) charge,  $Q_{\text{surf}}$ , associated with the trapping of electrons by protons should produce a measurable change,  $\Delta V_{\text{H}}$ , in the potential drop across the Helmholtz layer given by

$$\Delta V_{\rm H} = \frac{Q_{\rm surf}}{C_{\rm H}} \tag{7}$$

where  $C_{\rm H}$  is the Helmholtz capacitance. Under potentiostatic conditions, the potential drop across the space charge must decrease by an equal amount. The corresponding increase in space charge capacitance can be detected. In the present study, transient capacitance measurements were made at a modulation frequency of 10 kHz using a small time constant on the lock-in amplifier to allow adequate time resolution. Figure 10 illustrates the rising part of the transient capacitance response to an illumination step. The response can be fitted to a single exponential with a time constant of 3.3 ms, which is identical to the time constant for the microwave response.



**Figure 10.** Transient change in capacitance induced by step illumination of the p-Si(111) electrode. Potential = -1.6 V vs Ag|AgCl. Saturation photocurrent density =  $-3.0 \ \mu$ A cm<sup>-2</sup>. Measurement frequency = 10 kHz. The response can be fitted to a single-exponential rise with a time constant equivalent to  $k_1 = 30 \ s^{-1}$ . The increase in capacitance confirms that substantial light-induced surface charging occurs even at this very low photocurrent level.

The increase in capacitance shown in Figure 10 corresponds to a decrease in band bending of 180 meV. If we assume that this change in band bending arises from the surface charge associated with the H<sup>0</sup> intermediate (calculated from the analysis of the intensity dependence of the LMMR data discussed in the preceding section), we find a value of around 1  $\mu$ F cm<sup>-2</sup> for the Helmholtz capacitance. It is possible that this capacitance is associated not only with the electrolyte but also with a compensated surface layer arising from the ingress of hydrogen into the silicon. The reaction of hydrogen atoms to form dihydrogen may also occur near the surface and involve diffusion of hydrogen atoms between interstitial and defect sites. This conclusion is consistent with the observation of hydrogen ingress into p-Si.<sup>6,8,31</sup> Further work is required to clarify these aspects of the hydrogen evolution mechanism.

#### Conclusions

This study of hydrogen evolution at p-Si(111) has shown how a combination of steady-state and time|frequency resolved microwave reflectance measurements can be used to investigate photoelectrochemical reactions at semiconductor electrodes. The results demonstrate that a quantitative approach to interpretation of the steady-state light induced microwave reflectivity changes, based on modeling the electron and hole profiles, can be used to derive values of rate constants for electron transfer. These values of these rate constants can be compared with those obtained by analysis of the transient and periodic microwave reflectivity response. Differences between the values obtained by the two approaches can reveal kinetic complications such as multistep electrode reactions or effects such as reduced carrier mobility in the near-surface region. Despite the obvious power of the microwave technique, the mechanistic details of the hydrogen evolution reaction at p-Si have not been fully established, and further studies are required to identify the reaction steps and intermediates.

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