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

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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. The time and frequency resolved microwave responses show that interfacial electron transfer in this system is unusually slow. Comparison of the magnitude of the observed microwave response with theoretical predictions indicates that electron trapping occurs in the first step of the hydrogen evolution process, lowering the density of free electrons and hence the microwave response. The implications of this observation for the mechanism of the hydrogen evolution reaction are examined. The build up of high charge densities close to the surface as a result of slow electron transfer has been confirmed by transient photocapacitance measurements. Evidence is presented for light driven incorporation of protons and hydrogen into the near-surface region of the silicon.

Profiles of the electron and hole concentrations were used to calculate the mean change in conductivity as a function of experimental conditions and the rate constant for interfacial electron transfer. Comparison of the results with calculations of the microwave reactivity change based on solution of the Fresnel equations for a multilayer model confirmed that the microwave reflectivity change ΔR_M can be related linearly to the mean conductivity change ,<Δσ> by the expression

$$\Delta R_{\mathrm{M}} = \frac{P_{\mathrm{r}}}{P_{\mathrm{i}}} = R_{\mathrm{M}}\frac{\Delta P_r}{P_{\mathrm{r}}} = S < \Delta\sigma > = \frac{S}{d}\int_0^d \left[\mu_{\mathrm{n}}\Delta n(x) + \mu_{\mathrm{p}}\Delta p(x)\right]dx$$

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

The sensitivity factor relating the microwave response to the change in mean conductivity was determined for holes by measuring the potential modulated microwave response of the p-Si|NH_4F 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. The mean conductivity of the semiconductor electrode under depletion conditions can also be perturbed in the dark by changing the potential. The density of electrons and holes is negligibly small depletion region, so that

$$\Delta R_{\mathrm{M}} = S < \Delta\sigma > = \frac{Sq}{d}\mu_{\mathrm{p}} p_0 \Delta W_{\mathrm{sc}} = \frac{S}{d}\mu_{\mathrm{p}}\Delta Q_{\mathrm{sc}} = \frac{S}{d}\mu_{\mathrm{p}} C_{\mathrm{sc}}\Delta V$$

Here ΔW_{sc} is the change in the width of the space charge region, p_0 is the bulk hole concentration, ΔQ_{sc} is the change in the space charge, C_{sc} is the space charge capacitance and ΔV is the amplitude of the ac potential modulation. The linear relationship between the microwave and capacitance responses allows the sensitivity factor, S, to be determined experimentally and compared with calculations based on the Fresnel equations for a four layer model: air|bulk Si|depleted Si|solution.

The time constant for the response to step and sinusoidal illumination profiles is given by

$$\tau = \left(k_1 + k_{\mathrm{rec}}\right)^{-1}$$

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

$$k_1 = \frac{k_{\mathrm{tr}}}{\delta} = \frac{k_2 N_{\mathrm{redox}}}{\delta} = v_{\mathrm{th}}\sigma_{\mathrm{redox}} N_{\mathrm{redox}}$$

. Figure 1 compares the photocurrent and microwave response for p-Si in NH_4F. The slow decay of the microwave at the end of the illumination step is attributed to hydrogen egress from the near surface region. Figure 2 shows the microwave response on an expanded time scale. The rate constant for electron transfer is obtained from the exponential fit. The value of the first order rate constant is found to be 30 s^{-1}, which corresponds to k_{tr} = 3 × 10^{-6} cm s^{-1}. However the magnitude of the measured microwave response is two orders of magnitude smaller tan expected fro this value of k_{it}. The discrepancy is attributed to the fact that the hydrogen evolution reaction is a two-step process, involving formation of $H^{\cdot}$ as an intermediate.

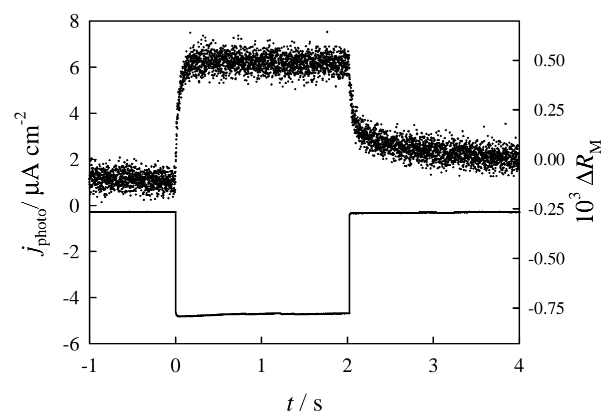

Figure 1. Photocurrent (lower plot) and microwave (upper plot) responses to a light step for p-Si in 1 M NH_4F (pH 3.0) at –1.0 V vs. Ag|AgCl.

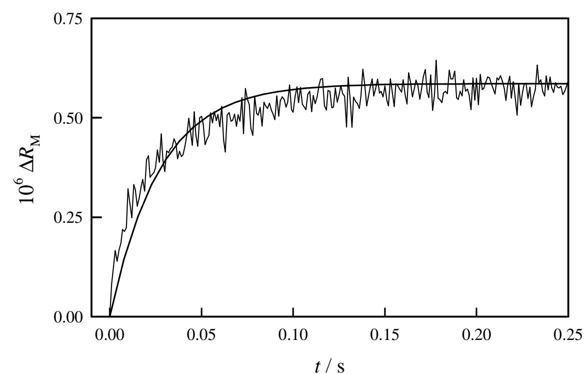

Figure 2. Exponential fit used to derive the rate constant k_1 from the microwave response.