Microwave Reflectance Studies of Photoelectrochemical Kinetics at Semiconductor Electrodes. Steady State, Transient and Periodic Responses

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Light and voltage induced changes in the microwave reflectivity of semiconductors can be used to study the kinetics of electron transfer at semiconductor|electrolyte interfaces. The method, which was pioneered by Tributsch and co-workers[1], is based on detection of photogenerated minority carriers 'queuing' at the interface. The theory of the method has been developed and illustrated by numerical calculations of the steady state microwave response for low-doped silicon. The results define the range of rate constants that should be experimentally accessible. The time and frequency responses of light induced microwave reflectivity changes are considered, and it is shown that they can be used to derive values of electron transfer and recombination rate constants.

The photoinduced microwave reflectance change is defined in terms of the incident and reflected microwave power, P_i P_r, as

$$\Delta R_M = \frac{\Delta P_r}{P_{in}} = R_M \frac{\Delta P_r}{P_r}$$

Under ideal conditions, ΔR_M depends linearly on the change in mean conductivity

$$\Delta R_M = S < \Delta\sigma > = \frac{S}{d}\int_0^d \Delta\sigma(x)dx = \frac{Sq}{d}\int_0^d \left[\mu_n \Delta n(x) + \mu_p \Delta p(x)\right]dx$$

where S is a sensitivity factor, which can be calculated or determined experimentally

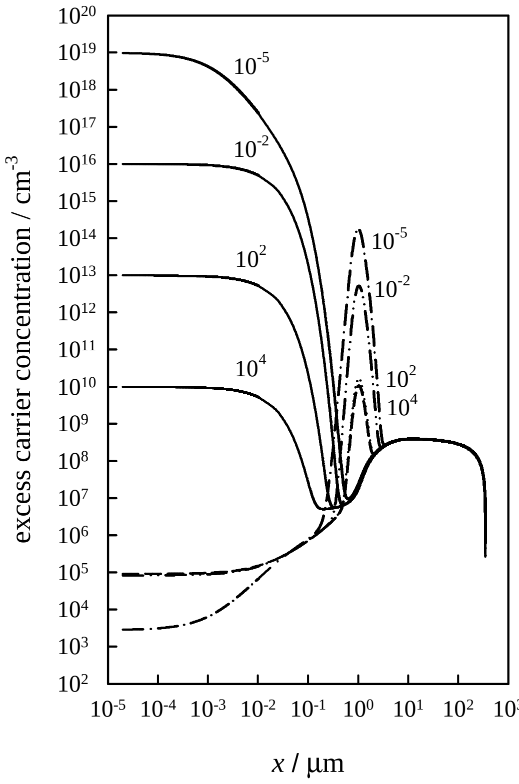
$\Delta<\sigma>$ can be calculated from the electron and hole profiles, which are obtained by solving the continuity equations numerically using the Hall Shockley Read approach to space charge recombination. Figure 1 illustrates the excess electron and hole profiles for low doped p-Si for a range of interfacial charge transfer rate constants. As expected, the concentration of electrons at the surface increases as the rate constant decreases.

Figure 2 shows the potential dependence of the microwave reflectance response calculated for different values of the electron transfer rate constant k_{tr}.. Again it is clear that the magnitude of the response depends on the rate constant: slow electron transfer leads to substantial build up of minority carriers and a correspondingly larger microwave response.

The microwave response can also be calculated from the Fresnel equations using a multilayer model to represent the carrier distributions. Figure 3 compares the result with the mean conductivity change. The inset shows the sensitivity factor for low doped p-Si is of the order of 1 Ω^{-1} cm for a variation of the electron transfer rate constant by five orders of magnitude

The theory has been extended to describe the time-dependent microwave response to stepped and sinusoidally modulated illumination, allowing independent measurement of k_{tr}.

1. Tributsch, H., *Modern Aspects of Electrochemistry*; White, R. E., Ed.; Kluwer Academic/Plenum publishers: New York, 1999; Vol. 33; pp 435.



1. Figure 1. Excess electron (continuous lines) and hole (broken lines) profiles for illuminated low doped p-Si under depletion conditions as a function of the rate constant k_{tr} (in cm s^{-1})

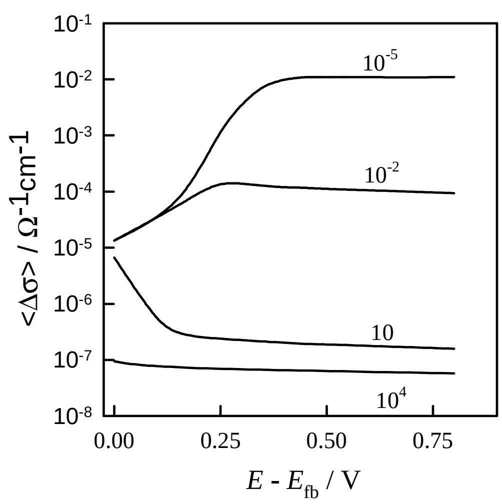


Figure 2. ΔR_M vs. potential for different values of k_{tr}.

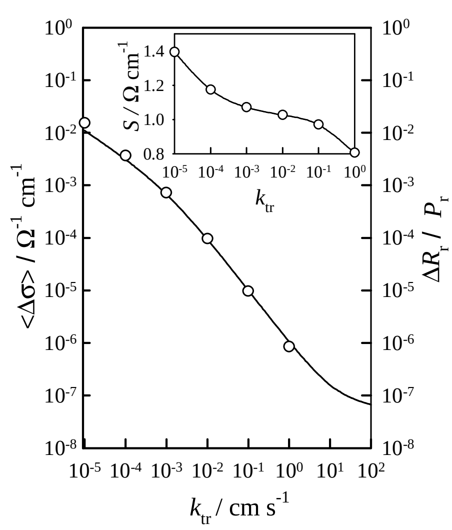


Figure 3. Continuous line – mean conductivity. Points ΔR_M from Fresnel model. Inset shows sensitivity factor.