Applications of Microwave Reflectance Methods to the study of Silicon (Photo)electrochemistry in Fluoride Solutions

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Microwave reflectivity measurements are used routinely to obtain information about minority carrier lifetimes and surface recombination velocities. In spite of this, however, applications of microwave methods in semiconductor electrochemistry are not widespread. More than a decade has passed since Tributsch and co-workers pioneered the application of microwave methods to study semiconductor electrodes systems [1-3], but their novel approach has been extended by only a handful of groups, including our own [4-6]. In this contribution we illustrate the versatility of microwave reflectance methods and highlight the types of information that they can provide.

Conventional methods of studying electrode processes at metal electrodes usually rely on time or frequency resolved electrical measurements. Electrical perturbation of the system is straightforward since the rate constants for electron transfer are potential dependent quantities. In the case of semiconductor electrodes, electron transfer reactions may involve electrons or holes generated by illumination. Optical perturbation of the system is then the most appropriate method because the rate constants for interfacial electron transfer may not be affected by changes in electrode potential. However, optically induced currents may not give information about interfacial electron transfer. Illumination produces electron hole pairs that are separated by the electrical field in the space charge region, and minority carriers (holes for n-type materials and electrons for p-type materials) are driven to the interface where they can take part in electron transfer reactions. Under steady state conditions, the rate of arrival of carriers at the interface is equal to the rate of electron transfer. This means that the photocurrent is simply determined by the rate of photogeneration of minority carriers, so no information about the kinetics can be obtained. The situation is no better under non steady state conditions, where the flux of minority carriers into the surface is balanced by electron transfer and charging of the space charge capacitance. The two processes cannot be separated in the photocurrent in the external circuit, which simply follows the shape of the light pulse if RC effects are negligible. Our work has shown that this limitation of methods based on light perturbations can be overcome if some of the minority carriers recombine with majority carriers at interfacial sates ('surface states'). The occurrence of surface recombination induces a flux of majority carriers into the surface states. The measured photocurrent is then determined by the sum of the minority and majority carrier fluxes In this case the competition between interfacial electron transfer and surface recombination leads to a time (or frequency) dependence of the photocurrent that allows determination of the rate constants for surface recombination and electron transfer. This is the basis for the use of intensity modulated photocurrent spectroscopy (IMPS) in studies of photoelectrochemical kinetics.

In the absence of surface recombination, IMPS cannot be used to obtain kinetic information about minority carrier reactions, although it can be used to measure rate constants for the majority carrier injection processes that occur during photocurrent multiplication. By contrast, microwave reflectivity methods can still provide kinetic data under conditions where time and frequency resolved photocurrent measurements yield no information. The reason for this is that the microwave reflectivity of a semiconductor electrode is sensitive to perturbations of the majority and minority carrier densities in the semiconductor. As consequence, the build-up of minority carriers at the interface and their subsequent decay by charge transfer can be followed under non steady-state conditions.

Microwave reflectivity methods can also be used to study semiconductor electrodes in the dark. In this case the behaviour depends on whether the semiconductor|electrolyte junction is in depletion, accumulation or inversion. Under depletion conditions, perturbation of the electrode potential modifies the width of the space charge region, and the modulated microwave response is linearly related to the space charge capacitance. This allows deconvolution of the total interfacial impedance. Under accumulation and inversion conditions, potential modulation changes the density of majority carriers at the interface and the potential dependence of the microwave reflectivity can give information about the potential distributions across the system.

In this paper we illustrate the power of microwave reflectivity measurements carried out on p-Si in fluoride media. The experimental data are related to the results of theoretical calculations of the distribution of excess carrier densities through the sample under different conditions.

Acknowledgments

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