Photoelectrochemical Kinetics and Related Devices

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I. INTRODUCTION

Semiconductor photoelectrochemical kinetics is important practically because its application may give a system for the production of a storable fuel. The objective of the present chapter is to pick out very selectively and describe outstanding contributions which have been made in the last 20 years to this area and to indicate some needed areas of advance.

II. SOME IMPORTANT PAPERS IN PHO TOELECTROCHEMICAL KINETICS

1. Green: The Basic Dependence on Surface States

The first paper that we would like to mention here is not a photoelectrochemical paper, though it has remained the basis to much progress being done in that field. It is the paper of Mino Green,\textsuperscript{1,2} who was the first to write down the electrode kinetic equations which describe the changes of the double layer with the presence of various degrees of surface states at the semiconductor-solution interface.
Green's calculations led to the conclusion that in the absence of surface states (by which he meant less than about $10^{12}$ per cm$^2$), changes in the Helmholtz potential difference (p.d.) with electrode potential remain minimal, e.g., in the region of a few tens of millivolts. The p.d. within the semiconductor remains relatively large, about ten times that of the Helmholtz p.d.

The Fermi level in a doped semiconductor moves with the doping and remains near the conduction band for $n$-type and the valency band for $p$-type. Therefore the Fermi level moves about as the potential changes (Figs. 1 and 2), whereas in metals the Fermi level is pinned.

However, when there is a sufficient concentration of surface states, either due to the presence of adsorbed atoms on the semiconductor (as in hydrogen discharge) or due to the introduction of surface states (more probably) as a result of the adsorption of

\[ \text{O} \quad \text{VACUUM LEVEL} \]

\[ \text{CB} \quad \text{at } V_1 \quad \text{at } V_2 \]

\[ \text{CB} \quad \text{Ef}(1) \quad \text{Ef}(2) \quad \text{at } V_1 \]

\[ \text{VB} \quad \text{at } V_2 \]

\[ \text{ELECTROLYTE} \]

\[ \text{n-TYPE SEMICONDUCTOR} \]

\[ \text{(WITHOUT SURFACE STATES)} \]

Figure 1. Schematic diagram of $n$-type semiconductor–solution interface at two applied potentials, $V_1$ and $V_2$, in the absence of surface states. The diagram shows that the potential drop, p.d., in the Helmholtz layer exhibits no variation with applied potentials in this case of having no surface states. Fermi level is not pinned.