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The Theory of the Light-Induced Evolution of Hydrogen at Semiconductor Electrodes

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ABSTRACT

The photoelectrode kinetics of the hydrogen evolution reaction is considered, using the WKB approximation for the penetration of the barrier at the semiconductor-solution interface. The absorption characteristics of photons in the electrode are introduced and the number of electrons produced at the surface is obtained as a function of the semiconductor statistics, and also to the number of holes produced in the valancy band. From Eq. [3], \( N_e(x)dx \) is given by

\[
N_e(x)dx = N_h(x)dx - N_{ph}(x)dx
\]

where \( N_h(x)dx \) is the total number of holes produced in the valency band. From Eq. [4], \( N_e(x)dx \) is given by

\[
N_e(x)dx = N_h(x)dx - N_{ph}(x)dx
\]

Number of Electrons Arriving at the Electrode Surface

The electric field at the surface of a semiconductor is well known from the work of Kingston and Neuštäder (14). It is possible to extend their result in finding an expression for the field at any point within the semiconductor.
suggests that the energies of all the photoexcited elec-
with the energy of the exciting photons, Fig. 1 (16),
bottom of the conduction band. Thus, the average
It seems reasonable to postulate that this energy is the
so-called critical potential (i.e., the potential at which,
path length of an electron is 1/a ~ 10^-4 cm. A typical

\[
\left( \frac{dV}{dx} \right)_x = \pm \sqrt{\frac{8e\hbar kT}{e} \left[ -(N_D - N_A) y + \alpha (e^{-y} - 1) + \nu_0 (e^y - 1) \right]} \]

where

\[
y = \frac{e_0 (V_x - V_b)}{kT}
\]

and the + sign is for y < 0.

The number of photoexcited electrons, originally
expressed for x = x in Eq. (3) and (4), decreases to
\[ N_{e,x=\infty dx(x)} dx = N_e(x) e^{-dx} dx \]

where \( L(x) \), the mean free path of electrons at x, is
given by (5)

\[ L(x) = \sqrt{\frac{\hbar^2}{m_e^2 e^2}} \frac{1}{\sigma_{D}} \]

where \( \sigma_{D} \) is the diffusion length and \( \sigma_{E} \) is the drift
length. The terms \( \sigma_{D} \) and \( \sigma_{E} \) are given by(2)

\[ \sigma_{D} = \sqrt{\frac{3000 \text{mV} \tau_e kT/e_0}{V}} \]

\[ \sigma_{E} = \frac{\alpha \sqrt{V}}{\sigma_{D}} \]

respectively, where \( \alpha M \) is the mobility of the electron
\( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \), \( \tau_e \) is the lifetime of the electron, and
\( V' \) (x) is the potential gradient at x = -(dV/dx) x in V
\( \text{cm}^{-1} \).

Similarly

\[ N_{e,x=\infty dx(x)} dx = N_{e,x=x} dx \]

\[ \int_{x}^{x+dx} N_{e,x=x} dx = N_e(x) dx \]

[11]

After \( N \) steps (\( N = x/dx \)), at the surface

\[ N_{e,x=0} dx = N_{e,x=0} dx \]

\[ \int_{x}^{x+dx} N_{e,x=0} dx = N_e(x) dx \]

[12]

\[ N_{e,x=0}(x) dx \]

is the number of electrons excited be-
 tween x and x + dx arriving at the surface per unit
area per unit time. Therefore, the total number of
electrons arriving at the surface per unit area per unit
time \( N_e(h_0 V) \), is given by

\[ N_e(h_0 V) = \int_{0}^{\infty} N_{e,x=0}(x) dx \]

[13]

which represents all the electrons excited by photons
at any distance inside the semiconductor and which
reach the surface, where V is the p.d. inside the semi-

**The Energy of an Electron Arriving at the Surface**

The experimentally observed independence of the
so-called critical potential (i.e., the potential at which,
for light of a given wavelength, the current begins)
with the energy of the exciting photons, Fig. 1 (16),
suggests that the energies of all the photoexcited elec-
trons are the same by the time they reach the surface.
It seems reasonable to postulate that this energy is the
bottom of the conduction band. Thus, the average
path length of an electron is 1/a = 10^-4 cm. A typical

\( k \) and \( e_0 \) must be in gaussian units.
The image interaction, $U_{\text{lm}}(x)$, is given by

$$U_{\text{lm}}(x) = \frac{\varepsilon_0^2}{4\varepsilon_{\text{st}}} \left( \frac{e - \varepsilon}{\varepsilon + \varepsilon_{\text{st}}} \right)$$

Interaction with ions in the OHP and their images.—When a photoexcited electron leaves the semiconductor surface, it interacts with all ions in the OHP and their electrical images in the semiconductor. The Coulombic force between this electron ($x$ from electrode) and all ions in OHP and their images, $F(x)$, is given by (8)

$$F(x) = -\frac{\varepsilon_0^2}{4\varepsilon_{\text{st}}} \left( \frac{e - \varepsilon}{\varepsilon + \varepsilon_{\text{st}}} \right)$$

$$-\frac{2\pi\varepsilon_0^2}{\varepsilon_{\text{st}}} \sum_{n=1}^{\infty} \left\{ \frac{d - x}{(d - x)^2 + n^2R_i^2} \right\}^2$$

$$-\frac{(d + x)^2 + n^2R_i^2}{(d + x)^2 + n^2R_i^2} \left( \frac{e - \varepsilon}{\varepsilon_{\text{st}}} \right)$$

where $\delta$ is the distance between the electrode surface and the nearest proton of the H$_3$O$^+$ ion, $d_{OH}$ is the distance between hydrogen and oxygen atom in water, $d$ is the distance between the semiconductor surface and OHP, $\varepsilon_{\text{st}}$ is the static dielectric constant of water, $n = 1, 2, 3$ and represents the succession of rings of ions around a given central ion, and $R_i$ is the distance between two ions in the OHP, depending on their coverage. The potential barrier.—From the above considerations, the potential energy barrier for electron transfer, $U(x)$, from the surface of the semiconductor surface to the H$_3$O$^+$ is given by

$$U(x) = U_{\text{lm}}(x) + \int_{x}^{\infty} F(x) \, dx + e_d X_d x$$

where $X_d$ is the field in the double layer.

Potential Drop in the Semiconductor and in the Double Layer

The potential drop in the electric double layer at the SCSolution interface is often considered to be negligible (22). However, when the carrier density of the semiconductor is high, or the density of the surface states is high, the potential drop in the electric double layer cannot be ignored. We can obtain this quantity from an analysis of the Mott-Schottky plot (23, 24).

The Mott-Schottky relation is given by

$$\frac{1}{C_{\text{SC}}} = \frac{8\pi}{e_0n_A} \left( \frac{\psi_{\text{SC}} - kT}{e_0} \right)$$

where $C_{\text{SC}}$ is the space charge capacity, $N_A$ is the concentration of ionized acceptors, and $\psi_{\text{SC}}$ is the potential drop in the space charge layer.

The appropriate relation in the case of measurements in solution is

$$\frac{1}{C^2} = \frac{8\pi}{e_0n_A} \left( V - V_{\text{Frp}} - \frac{kT}{e_0} \right)$$

where $C$ is the total capacity of the electrode (neglecting the roughness factor) and $V$ and $V_{\text{Frp}}$ are the electrode potential and the flatband potential with respect to a reference electrode, respectively.

Since (see Fig. 2)

$$V - V_{\text{Frp}} = \psi_{\text{SC}} + \Delta \phi_H$$

* $C_{\text{SC}}$ has been assumed equal to $C_{\text{measured}}$ because other capacitances (e.g., that of the counterelectrode and Helmholtz layer) are much larger than $C_{\text{SC}}$ and hence negligible in series array.*
where
\[ \Delta \phi_{PH} = \left(3C \Delta \phi \right)_{V} - \left(3C \Delta \phi \right)_{fbp} \]  \[ [22] \]
and \( \Delta \phi \) is the Galvani p.d. in the double layer at \( V \) and the fbp, respectively, then, Eq. [21] becomes
\[ \frac{1}{C^2} = \left( \frac{8\pi}{e_{0}N_A} \right) \left( \psi_{SC} + \Delta \phi_{PH} - \frac{kT}{e_{0}} \right) \]  \[ [23] \]
Only when \( \Delta \phi_{PH} = 0 \) or \( \Delta \phi_{PH} = \psi_{SC} \) where \( c \) is a proportional constant, does the plot between \( (1/C^2) \) and \( V \) become linear (23, 24).
If \( \Delta \phi_{PH} = 0 \), Eq. [21] becomes Eq. [20] and the slope of the experimental plot (Eq. [21]) must be the same as that of the theoretical plot.
In the case of \( \Delta \phi_{PH} = \psi_{SC} \), Eq. [24] becomes
\[ \frac{1}{C^2} = \left( \frac{8\pi}{e_{0}N_A} \right) \left( \psi_{SC} + \frac{kT}{e_{0}} \right) \]  \[ [24] \]
and thus, \( c \) can be calculated by comparing the experimental slope with the theoretical one. This is the case found in recent experimental work (16). \( (V - V_{fbp})/(1 + c) \) gives the potential drop in the space charge layer in the semiconductor.
De Gryse et al. (25) criticized reasoning of this type by showing that the slope of the plot has the same value whether the potential drop occurred in the electric double layer or not. However, in their treatment they assumed an absence of surface charge and this assumption limits the applicability of the interpretation. The experimental pH dependence of the flatband potential can only be interpreted by assuming the existence of surface states, and the discussion of de Gryse et al. on this matter is no longer directly applicable to situations of this kind.

**Photocurrent Expression**

By taking into account the above considerations and Eq. [2], the photocurrent, \( i_p \), is given by
\[ i_p = \frac{C_A}{C_T} \int_{0}^{\alpha} N(E)W(E)G(E)dE \]
\[ = \frac{C_A}{C_T} \frac{N_{Ae}(hv_{SC})}{e_{0}} \exp \left(-\frac{\beta(\Delta H(e) + e_{0}\Delta \phi_{PH})}{kT} \right) \]  \[ [25] \]
where \( N_{Ae}(hv_{SC}) \) is the number of electrons arriving at the surface when the potential drop in the semiconductor is \( \psi_{SC} \) and can be obtained from Eq. [13] replacing \( V \) by \( \psi_{SC} \); \( U_{max} \) is the barrier maximum with respect to the bottom of the conduction band at the flatband potential; \( \Delta \phi_{PH} \) is defined in Eq. [22]; and \( V \) is defined in Eq. [21]. The use of \( e_{0}\Delta \phi_{PH} \) for the electron energy in the tunneling expression is consistent with a model in which the electrons arrive at a uniform energy at the bottom of the conduction band, i.e., \( E_{c} = 0 \); and the barrier is then influenced by the p.d. in the double layer in the sense that the barrier is reduced when \( \Delta \phi_{PH} \) is negative.5,6

**Computation of the Photocurrent-Potential Relation and Comparison with Experimental Results**

Photocurrents were calculated for the example of GaP for different wavelengths of light as a function of potential. A schematic energy diagram, which shows the shape of the barrier, is shown in Fig. 3. It was constructed by the use of Eq. [16] and [17] in Eq. [18].

The values used for the calculation of \( i_p \) through such a barrier by the use of [25] are: \( \tau_{e} = 10^{-6} \) sec (26), \( \mu_{e} = 300 \text{ cm}^{2} / \text{V sec} \) (27), \( n_{e} = -11.5 \text{ eV} \) (28), \( E_{b} = 4.3 \text{ eV} \) (27), \( J = 13.6 \text{ eV} \) (28), \( A = -0.3 \text{ eV} \) (29), \( R = -0.1 \text{ eV} \) (30), \( \epsilon = 11 \) (31), \( E_{b} = 2.25 \text{ eV} \) (27), \( V_{fbp} = 1.13 \text{V} \) (NHE) (16), and \( c = 1.32 \) (16).

Equation [25] is no longer an integral because transfer is seen as occurring only from electrons at the bottom of the conduction band (i.e., photogenerated electrons have been deactivated until they arrive at the interface at a potential \( V_{fbp} \)).

A rough computation for GaP-NaOH at 0 on the NH scale suggests that about 85% of the electrons activated by light reach the surface. Those which do not tunnel to the solution deactivate at the surface in the valence band.

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4 In general, the p.d. at a semiconductor-solution interface will be partly in the solution if the doping is very high or there is a significant concentration of surface states.

5 Equation [25] is no longer an integral because transfer is seen as occurring only from electrons at the bottom of the conduction band.

6 A rough computation for GaP-NaOH at 0 on the NH scale suggests that about 85% of the electrons activated by light reach the surface. Those which do not tunnel to the solution deactivate at the surface in the valence band.

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**Fig. 3. Schematic diagram of the potential energy barrier for electron transfer from GaP electrode at flatband potential to an acceptor. (\( E_{b} \) is the energy gap; critical potential = potential at which photocurrent commences.)**

**Discussion of Discrepancies Between Theory and Experiment**

Discrepancies between theory and experiment exist as follows:
1. Theoretically estimated quantum efficiencies are only 20-30% of the experimental quantum efficiencies.
2. The position of the theoretical quantum efficiency-potential relations appear at about 0.2-0.4 V more positive than those of experiment.

These discrepancies may be due to cumulative uncertainties in the quantities of Eq. [17] which give the energy levels of electrons in the neutralized \( \text{H}_{2}\text{O}^{+} \); \( \Delta H(e) \) at the flatband potential and uncertainties in the value of the barrier width, which has been taken as \( 0.01 \sim 0.2 \text{ eV} \). Were this taken into account, the theoretical quantum efficiency-potential relations would shift toward more negative potentials (i.e., an improvement) by 0.01-0.2 V, depending on the carrier density.
than those calculated in the present model would be expected.

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32. J. O'M. Bockris and K. Uosaki, Paper submitted to This Journal.

Fig. 4. Calculated and experimental quantum efficiency vs. electrode potential curves for GaP in 1N NaOH at the three monochromatic wavelengths (a) 4500; (b) 4000; and (c) 3500.

In respect to the determination of the barrier dimension, the electron was assumed to transfer to a proton in the second layer of water, to which a proton transfers from H₂O⁺ in the OHP prior to electron transfer (28). However, it may be possible that a proton transfers to water attached to the electrode surface, and electrons transfer to that. In this case, the barrier thickness becomes much smaller than that assumed and, therefore, higher quantum efficiency

The origin of this model lies in the interpretation of the values observed for the dependence of the separation factor on the potential (11). Much lower barrier widths give separation factors which are too large.