THE INFLUENCE OF ELECTROLYTIC MASS TRANSFER ON THE PERFORMANCE OF PHOTOELECTROCHEMICAL CELLS

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A one-dimensional mathematical model of a photoelectrochemical cell is developed which accounts explicitly for the transport, generation, and recombination of electrons and holes in the semiconductor, the coupling among interfacial reactions, and transport of electrolytic species by diffusion, migration, and convection. This model is used to show the degree of coupling expected between processes taking place in the semiconductor and in the electrolyte. The influence of electrolytic mass transfer was evaluated for an n-type GaAs semiconductor in contact with a 0.80 M K$_2$Se$_2$, 0.10 M K$_2$Se$_3$, 1.0 M KOH electrolyte. Calculated current-potential curves were shown to be relatively unaffected by limitations to electrolytic mass transfer, even at large fractions of the limiting current. The magnitude of charge held within the electrolytic double layer and the space-charge region of the semiconductor is relatively invariant for currents significantly below the limiting current, but increases as the mass-transfer-limited current is approached. The hole concentration at the semiconductor-electrolyte interface increases as kinetic and mass-transfer limitations to interfacial reactions are approached. The implications of these results for the stability of photoelectrochemical cells and for the application of photoelectrochemical techniques to semiconductor processing are discussed.

KEYWORDS Semiconductor electrodes Photoanodes Mathematical model.

INTRODUCTION

Semiconducting electrodes have been studied as a means of converting solar energy to chemical or electrical energy. The liquid-junction photovoltaic cell, an electrochemical system with one or two semiconducting electrodes, is an appealing system for this purpose. In these cells, the electric contact between the solid and the electrolyte is achieved easily and simply in comparison to that of a solid-state device. The band bending necessary for the photovoltaic processes at the interface is created by the redistribution of charge at the semiconductor-electrolyte interface upon immersion of the semiconductor. In contrast, $p-n$ junctions are typically fabricated through high-temperature diffusion of dopants in single crystals. Due to the ease of fabrication, photoelectrochemical cells have been considered to be economic alternatives to solid-state solar cells.

The principal limitation to the use of photoelectrochemical cells for solar energy conversion is that semiconductors with a bandgap appropriate for efficient conversion of the solar energy (i.e., 1.0 to 1.5 eV) tend to corrode easily when illuminated. This problem, however, can be alleviated by using more stable
semiconductors (i.e., those with bandgap of 4–5 eV), or by using an \textit{n}-type semiconductor such as \textit{n}-GaAs in contact with a redox couple such as \( \text{Se}_2^{2-}/\text{Se}^{2-} \). The success of the later approach is due to the ease with which the redox couple competes with the photo-corrosion reactions for holes in \textit{n}-type GaAs electrodes\textsuperscript{14} to prevent photodissolution of the semiconductor. The use of large bandgap semiconductors, while effective in reducing the extent of photodissolution, results in low-efficiency devices because most of the solar energy spectrum is not converted.

The energetics and kinetics of photo-induced charge-transfer reactions across the semiconductor-electrolyte interface have stimulated a large international research effort in the last decade since Honda and coworkers\textsuperscript{6} first pointed out the potential applications of photoelectrochemical systems for solar energy convergence and storage (see references 6–17 for reviews of this field). In more recent years, photoelectrochemical cells have been investigated for semiconductor processing. This method provides an alternative technique for the direct maskless etching of III–V and II–VI semiconductors\textsuperscript{18–23} and for the direct plating of metals onto high-density chips.\textsuperscript{24} This method is a low-temperature liquid-phase technique, ideal for compound semiconductors (e.g., GaAs) which decompose at temperatures required for more conventional lithographic methods that involve vapor-phase etching.\textsuperscript{25,26} In contrast to photo-assisted vapor-phase processing, the photoelectrochemical process involves generation of electron-hole pairs in the illuminated semiconductor. Thus, a broad-band incoherent light source can be used since all photons with energy greater than the band-gap energy are effective in generating minority carriers. The use of an incoherent light source is attractive for the rapid processing of large areas. Lasers could be used to generate interference patterns at the substrate surface.\textsuperscript{27–29} The effect of illumination is to generate potential and concentration driving forces for electrochemical reactions (either etching or plating).

Applications of this technology to the fabrication of electronic devices requires determination of the relationship between processing and design parameters and the rate of electrochemical reactions. Considerations such as counterelectrode placement, electrolyte composition, and illumination intensity are unique to photoelectrochemical processing, and these parameters can be expected to have a major influence on the resolution of this technology.

Most experimental and theoretical studies of photoelectrochemical cells have emphasized the role of the semiconductor and the semiconductor-electrolyte interface.\textsuperscript{5–13} This is due, in part, to the experimental observation that the stirring of the electrolyte has little effect on the terminal characteristics of these cells. Electrolytic mass transfer, however, can play an important role in the photoelectrochemical etching of the semiconductors. Therefore, to explore the influence of electrolytic mass-transfer on the behavior of a photoelectrochemical cell, a mathematical model was developed for a rotating semiconductor disk electrode which accounts explicitly for the transport, generation, and recombination of electrons and holes in the semiconductor, the coupling among interfacial reactions, and mass-transfer of electrolytic species by diffusion, migration, and convection. The influence of electrolytic mass-transfer was evaluated for an
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$n$-type GaAs semiconductor in contact with a $0.80 \text{ M } \text{K}_2\text{Se}$, $0.10 \text{ M } \text{K}_2\text{Se}_2$, $1.0 \text{ M } \text{KOH}$ electrolyte. This work applies strictly to a photoelectrochemical cell used for solar energy conversion; however it may be regarded to be a first step toward the analysis of photoelectrochemical processing of semiconductors.

DESCRIPTION OF THE CELL

The principal elements of a photoelectrochemical cell are shown in Figure 1. This cell consists of the counterelectrode, the current-collector, the semiconductor, the electrolyte, and the semiconductor-electrolyte interface. The counterelectrode was assumed to be sufficiently large and far from the electrode that it did not influence the current distribution. The cell potential calculated in this work corresponds to a photovoltage measured between the current-collector and a reference electrode located at the outer limit of the diffusion layer. The interfacial region, taken as a whole is electrically neutral. Charge associated with the interfacial planes must, therefore, be balanced by diffuse regions of charge adjacent to these planes. The thickness of these regions of charge is characterized by the Debye length which has a value of order $200 \text{ Å}$ for the space-charge region of the semiconductor and $2 \text{ Å}$ for the diffuse part of the electrolytic double layer. The characteristic length for the diffusion layer is about $10^6 \text{ Å}$. the tremendous variation of the characteristic lengths for these regions requires the systems of equations be developed for each region and matched at appropriate locations by continuity relationships.

FIGURE 1 Schematic representation of the photoelectrochemical cell. Scaling lengths are approximate and depend upon operating conditions. Interfacial planes are represented by OSS, outer surface states; ISS, inner surface states; IHP, inner Helmholtz plane; OHP, outer Helmholtz plane.
THEORETICAL DEVELOPMENT

This work extends the treatment of Orazem and Newman\(^{30-32}\) to account explicitly for electrolytic mass transfer to the semiconducting electrode. Macroscopic transport equations were used to characterize the electrolyte and the semiconductor phases. These were used in conjunction with a microscopic model of the semiconductor-electrolyte interface which couples the governing equations between these bulk phases. The coupled equations which govern the semiconductor, the semiconductor-electrolyte interface, and the electrolyte (see Figure 1) were solved numerically. Development of the equations which govern the semiconductor and the semiconductor-electrolyte interface is presented only briefly below; they are covered in more detail in references 30 and 32.

Semiconductor

The flux of electrons and holes in the semiconductor can be treated within the framework of dilute-solution theory. For a one-dimensional system and under the steady-state assumption, the flux of holes \(N_{h,z}\) is given by

\[
N_{h,z} = -u_h p F \frac{d\Phi}{dz} - D_h \frac{dp}{dz},
\]

and a similar result is obtained for the flux of electrons. The concentrations of electrons and holes are represented by \(n\) and \(p\), respectively, and the mobilities \(u_i\) are related to the diffusivities \(D_i\) by the Nernst–Einstein equation; i.e.

\[
D_i = RT u_i.
\]

The material balance for holes is written

\[
\frac{dN_{h,z}}{dz} = R_h,
\]

where \(R_h\) is the net rate of production of holes under steady-state conditions. The rate of production of holes is, by stoichiometry, equal to the rate of production of electrons and is governed by three concurrent processes: generation by absorption of light, generation by absorption of heat, and recombination of electrons and holes (i.e., transfer of an electron from the conduction band to the valence band). Electron-hole recombination was assumed to take place through uniformly distributed trap states as well as by a band-to-band mechanism. This model results in

\[
R_h = \eta m q_0 e^{-mz} - \frac{N_h k_2 (np - n_i^2)}{k_4 (k_1 N_u + k_3 N_v + k_2 p) + n},
\]

where \(k_1, k_2, k_3,\) and \(k_4\) are the rate constants for reactions corresponding to transfer of electrons from the valence band to the trap energy, the trap to the conduction band, and the conduction band to the trap, respectively, and \(n_i\) is the intrinsic concentration for the semiconductor.
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Under steady state conditions the fluxes of holes and electrons are related by

$$\frac{dN_e}{dz} - \frac{dN_h}{dz} = 0. \quad (5)$$

A material balance on electrons, analogous to Eq. (3), could be used to replace Eq. (5); however, numerical computational accuracy is enhanced by coupling conservation of the minority carrier with Eq. (5).

Poisson’s equation,

$$\frac{d^2\Phi}{dz^2} = -\frac{F}{\varepsilon_{sc}} \left[ p - n + (N_d - N_a) \right], \quad (6)$$

relates the potential to the charge distribution. The Debye length,

$$\lambda_{sc} = \left[ \frac{\varepsilon_{sc}RT}{F^2(N_d - N_a)} \right]^{1/2}, \quad (7)$$

characterizes the distance over which the potential varies in the semiconductor. It typically has a value of $1 \times 10^{-6}$ to $2 \times 10^{-5}$ cm.

Semiconductor-Electrolyte Interface

The rate expression used for the general interfacial reaction $l$,

$$\sum_i s_i M_i^l \rightarrow 0, \quad (8)$$

was given by

$$r_i = k_{f,i} \exp \left[ \frac{(1 - \beta_i)nF\Delta\Phi_i}{RT} \right] \prod_l c_i^{p_i,l} - k_{b,i} \exp \left[ \frac{-\beta_i nF\Delta\Phi_i}{RT} \right] \prod_l c_i^{q_i,l}, \quad (9)$$

where $\beta_i$ is a symmetry factor assumed here to be equal to $1/2$, $k_{f,i}$ and $k_{b,i}$ are forward and backward reaction rate constants, respectively, $n$ is the number of electrons transferred, and $\Delta\Phi_i$ is the potential driving force for the given reaction, $l$. The potential driving force enters into reactions involving charge transfer from locations of one potential to locations of another. The reaction orders for a given species $i$ in the forward and reverse directions are $p_{i,l}$ and $q_{i,l}$, respectively. These reaction orders are equal to zero except that $p_{i,l} = s_{i,l}$ for a species that appears as a reactant in Eq. (8) ($s_{i,l} > 0$) and $q_{i,l} = -s_{i,l}$ if $s_{i,l} < 0$.

The reaction rates are related to surface concentrations by material balances written for each adsorbed species at the interfacial planes ISS and IHP. Gauss’s law was applied to the interfacial planes to relate the potential to the charge held at these planes.

Electrolyte

Dilute solution theory with constant fluid properties, transport properties, and activity coefficients was assumed to apply to the electrolyte. The flux density of an
ionic species was expressed in terms of diffusion, migration, and convection by
\[ N_{i,z} = -z_i u_i F c_i \frac{d\Phi}{dz} - D_i \frac{dc_i}{dz} + c_i \nu_z. \]  
(10)

Equation (10) applies to both the diffuse part of the double layer close to the electrode and the diffusion layer far from the electrode. Continuity for each species \( i \) requires that in the absence of homogeneous reactions
\[ \nabla \cdot \vec{N}_i = 0. \]  
(11)

The velocity distribution close to the surface of a rotating disk electrode is given by
\[ v_z = \sqrt{\Omega \nu (-0.50123 \zeta^2 + \frac{1}{3} \zeta^3 + 0.10267 \zeta^4 + \cdots)}, \]  
(12)
where \( \zeta = z \sqrt{\Omega / \nu} \). This expression can be used here because the Schmidt number, \( Sc = \nu / D_l \), is large for electrolytic solutions. Within the diffuse part of the double layer, the potential is related to the charge held in solution by Poisson's equation, i.e.,
\[ \frac{d^2 \Phi}{dz^2} = -\frac{F}{\epsilon_{sol}} \sum_i z_i c_i. \]  
(13)

The scaling length for this region is the Debye length, i.e.,
\[ \lambda_{sol} = \left[ \frac{\epsilon_{sol} RT}{F^2 \sum_i z_i^2 c_i} \right]^{1/2}. \]  
(14)

The solution outside the diffuse double layer can be assumed to be electrically neutral, therefore, Poisson's equation can be replaced by
\[ \sum_i z_i c_i = 0, \]  
(15)
in the diffusion layer. The scaling length for this region is given by
\[ \delta = \sqrt{\nu / \Omega} \left( \frac{3D_l}{0.51023 \nu} \right)^{1/3}. \]  
(16)

NUMERICAL METHOD

The coupled non-linear ordinary differential equations were properly linearized, posed in finite-difference form, and solved numerically for the cell at equilibrium and under steady-state conditions using Newman's BAND method coupled with Newton–Raphson iteration. A unique feature of this model is that the coupling between the diffuse part of the double layer and the diffusion layer allows efficient and accurate numerical solution of equations for regions characterized by scaling lengths that differ by five orders of magnitude. The efficiency of the calculations is further enhanced by local matrix inversion routine that reduces the large
number of equations to a set of equations involving only bulk variables. The convergence depended upon initialization but generally required less than 10 iterations. More detail on these aspects of the numerical technique is presented in reference 35.

The parameters used for this study and more detail on the model can be found in references 30–32. The difference between this work and that presented previously lies in the treatment of the diffusion layer. Electrolytic mass transfer at the semiconducting electrode in the modal presented by Orazem and Newman30,31 can be characterized by a diffusion layer of the same thickness as the diffuse double layer. The results obtained in their work are obtained here for large rotation speeds.

RESULTS AND DISCUSSION

The influence of kinetic and mass-transfer limitations was explored for a rotating n-GaAs disk electrode under AM-2 illumination and in contact with a selenium redox couple. The resulting current-potential curves are presented in Figure 2. Curve a was obtained in the absence of kinetic and mass-transfer limitations. Under kinetic limitations to charge-transfer reactions the current-potential curve shows an inflection point (see curve b). Limitations to electrolytic mass-transfer due to a reduced rotation speed (curve c) or a reduced bulk concentration (curve d) have little influence on the current-potential curve except at the limiting

![Figure 2](image_url)
current. The increase in the open-circuit potential observed for curve \( d \) is due to an increase in the charge held in the diffuse part of the double layer.

The reduction in cell potential due to limitations to electrolytic mass-transfer is significantly less than that predicted by standard expressions for the concentration overpotential. At 99.1 percent of the limiting current (curve \( c \)) the reduction in the cell potential is estimated to be \(-166.7\) mV. The corresponding value obtained in this study was \(-38.7\) mV. Limitation to electrolytic mass-transfer has less effect on the current-potential curve than it would for a strictly electrochemical system because the decrease in electrolytic concentration driving force for the surface reactions is compensated by increases in concentration and potential driving forces in the semiconductor.

Kinetic and mass-transfer limitations significantly influence the distribution of electrons and holes in the semiconductor. The distribution of electrons and holes is presented in Figures 3, 4, 5, and 6 for the equilibrium condition (curves \( a \)), open-circuit under illumination (curves \( b \)), and near short-circuit (curve \( c \)).

In the absence of kinetic or mass-transfer limitations (Figure 3) the concentration distribution for electrons and holes approaches the equilibrium distribution as short-circuit is approached. In contrast, the surface concentration of holes increases greatly under kinetic or mass-transfer limitations (see curve \( c \) in Figure 4, 5, and 6 respectively). This has implications in photoelectrochemical processing.

![Figure 3](image-url)

**FIGURE 3** Calculated electron and hole concentration as functions of position for a rotating \( n \)-GaAs disk electrode in contact with a selenium redox couple with no kinetic or mass-transfer limitations. Curve \( a \), open-circuit without illumination (i.e., equilibrium); curve \( b \), open-circuit under illumination; curve \( c \), under illumination near short-circuit (\( I = 23.1 \text{ mA/cm}^2 \)).
where kinetic or mass-transfer limitations to the desired etching reactions limit the resolution of the technique. The increase in hole concentration over the equilibrium value creates a driving force for lateral diffusion of holes and a corresponding spread of the etching reaction distribution. An interesting result of this work is that mass transfer has the same effect even when current-potential curves do not show a dramatic influence of mass-transfer limitations. Kinetic and mass-transfer limitations also have a significant effect on the charge held within the space-charge region of the semiconductor and the diffuse part of the double layer. As shown in Figure 7, the charge distribution may be considered to be independent of current density only in the absence of kinetic or mass-transfer limitations. The increase of charge in the space-charge region under kinetic or mass-transfer limitations is consistent with the increase in hole concentration observed in Figure 3, 4, 5, and 6.

The electrolytic concentration distributions corresponding to curve c of Figure 2 are presented in Figure 8 for open circuit under illumination (dashed lines) and near limiting current (solid lines). The concentration of Se\(^{2-}\) approaches zero in the diffusion layer although it increases slightly in the diffuse part of the double layer. The difference in scale between the diffuse part of the double layer and the diffusion layer is evident in that the concentration derivatives are equal at the interface between the two regions. The concentrations at the semiconductor-
FIGURE 5 Calculated electron and hole concentration as functions of position for a rotating n-GaAs disk electrode in contact with a selenium redox couple with limitation to interfacial mass-transfer ($\Omega = 1.9$ rpm). Curve $a$, open-circuit without illumination (i.e., equilibrium); curve $b$, open-circuit under illumination; curve $c$, under illumination near the short-circuit ($i = 23.0$ mA/cm$^2$).

electrolyte interface differ from the bulk values because of the charge held in the diffuse part of the double layer. As shown in Figure 7, explicit treatment of this region is necessary under conditions of kinetic or mass-transfer limitation.

The key result of this work is that the conditions in the electrolyte (either small values for rate constants or small values for rotation speed) influence the distribution of electronic species in the semiconductor. This coupling can be attributed to the boundary conditions at the semiconductor-electrolyte interface where rates are expressed as functions of potential and concentrations of ionic species on the electrolyte-side of the interface and holes on the semiconductor-side. As long as the rate expression is a function of electron or hole concentration, this coupling is independent of the reaction mechanism chosen. For example, even simple rate expressions that are first order in holes show an increase in hole concentration for small rate constants. Validation of this result is given by the experimental observation of Rose et al.\textsuperscript{37} that a reduction in stirring speed caused the hole etched by a focused laser to increase in size, i.e., reduced the resolution for photoelectrochemical etching. The results presented here suggest that mass-transfer limitations for a reacting ionic species or for removal of a corrosion product could increase the hole concentration at the surface. The driving force for lateral diffusion would thereby be increased, and
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FIGURE 6 Calculated electron and hole concentration as functions of position for a rotating n-GaAs disk electrode in contact with a selenium redox couple with limitations to electrolytic mass-transfer ($\Omega = 1000$ rpm, $C_{\text{Se}^2^\cdot} = 0.0047$ M, and $C_{\text{Se}^4^\cdot} = 0.0367$ M). Curve a, open-circuit without illumination (i.e., equilibrium); curve b, open-circuit under illumination; curve c, under illumination near short-circuit ($i = 22.6$ mA/cm²).

the etching reaction, proportional to the surface hole concentration, would spread into unilluminated areas. Heller and Miller also report that the photocurrent stability of a n-CdSe photoelectrochemical cell is improved by stirring the electrolyte. Their result supports the argument that increases in hole concentration at the interface associated with mass-transfer limitations to the redox species increase the rate of the corrosion reaction.

CONCLUSIONS

A mathematical model of a photoelectrochemical system was developed which treats explicitly the semiconductor, the semiconductor-electrolyte interface, the diffuse part of the electrolytic double layer, and the diffusion layer in terms of potential and concentrations of charged species. Restrictive assumptions were avoided by the use of numerical solution of the governing equations. The results of the model show that mass-transfer limitations to electrolytic species do not affect significantly the calculated current-potential curves even at large fractions of the limiting current. Kinetic limitations, however, have a dramatic effect. Both kinetic and mass-transfer limitations to interfacial reactions give rise to a dramatic
FIGURE 7 Calculated charge as a function of current density for a rotating n-GaAs disk electrode in contact with a selenium redox couple. Curve $a$, in the absence of kinetic or mass-transfer limitations; curve $b$, interfacial kinetics are limiting; curve $c$, electrolytic mass-transfer is limiting ($\Omega = 1.9$ rpm); curve $d$, electrolytic mass transfer is limiting ($\Omega = 1000$ rpm, $C_{Se^2-} = 0.0047$ M and $C_{Se^6^-} = 0.0367$ M).

FIGURE 8 Calculated concentration distribution for electrolytic species for a rotating n-GaAs disk electrode in contact with a selenium redox couple with limitation to electrolytic mass-transfer ($\Omega = 1.9$ rpm). Dashed lines, open-circuit under illumination; solid lines, under illumination near short-circuit ($i = 23.0$ mA/cm$^2$).
increase in the hole concentration at the semiconductor-electrolyte interface. This result is consistent with the observation that the amount of charge held in the space-charge region of the semiconductor increases in magnitude as the mass-transfer-limited current is approached.

This model confirms the experimental observation that, below the limiting current, mass-transfer has very little effect on the terminal characteristics of the system, whereas kinetic limitations can severely limit power conversion efficiency. If power conversion is the focal point in the study of photoelectrochemical cells, the stirring of the fluid would have very little influence on the performance of the system. On the other hand, an increase in the interfacial hole concentration caused by kinetic or mass-transfer limitations provides a driving force which can enhance the rate of side reactions such as the semiconductor corrosion. Furthermore, this increase in the interfacial hole concentration can limit the resolution of photoelectrochemical techniques for semiconductor processing.

NOMENCLATURE

\( c_i \) molar concentration of species \( i \), mol/cm\(^3\)
\( D_i \) diffusivity of species \( i \), cm\(^2\)/s
\( F \) Faraday's constant, 96,487 C/equiv
\( m \) solar absorption coefficient, cm\(^{-1}\)
\( n \) electron concentration, mol/cm\(^3\)
\( N_c \) effective density of conduction-band states, mol/cm\(^3\)
\( N_t \) effective density of trap states, mol/cm\(^3\)
\( N_v \) effective density of valence-band states, mol/cm\(^3\)
\( \bar{N}_i \) flux of species \( i \), mol/s cm\(^2\)
\( p \) hole concentration, mol/cm\(^3\)
\( q_0 \) incident solar flux, mol/s cm\(^2\)
\( R \) universal gas constant, 8.3143 J/mol K
\( T \) absolute temperature, K
\( u_i \) mobility of species \( i \), cm\(^2\)/mol/J s
\( v_z \) axial velocity of the fluid, cm/s
\( z_i \) charge number of species \( i \)

Greek Symbols

\( \Phi \) electrical potential, V
\( \varepsilon \) permittivity, C/V cm
\( \eta \) photon efficiency
\( \lambda \) Debye length, cm
\[ \delta \] Characteristic length for mass transfer, cm
\[ \nu \] kinematic viscosity, \( \text{cm}^2/\text{s} \)
\[ \Omega \] rotation speed, 1/s

Subscripts
\[ \infty \] associated with the bulk
\[ \text{sol} \] associated with the solution
\[ \text{sc} \] associated with the semiconductor

REFERENCES