

**Figure 1.** Differences in average valence-shell energies between atoms A and the H atom (hartree). Left side: Free atoms F, O, and N relative to H as zero reference. Right side: Atoms F, O, and N in their hydrides relative to H in  $H_2$  as zero reference. Values for both left and right sides are per bond (pattern shown is not qualitatively altered if whole-molecule energies are employed). If the electronic chemical potential,  $\mu$ , were plotted in the same manner, the left side would be approximately the same, but the right side would be a single point at the reference line,  $H_2$ . Equalization of electronegativity does not occur.

each other, are required to have a common chemical potential,<sup>11</sup> in contrast to  $\chi_{\text{spec}}$  and other definitions of  $\chi$ ,

(11)  $\mu = -(I_{\text{min}} + A_{\text{max}})/2$ , where  $I_{\text{min}}$  and  $A_{\text{max}}$  are the minimum and maximum of the two  $I$  and  $A$  values, respectively. Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691. Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford Univ. Press: New York, 1989; Chapter 10.

which have free-atom values at infinite internuclear separation.

It is well-known that almost all chemical bonding phenomena can be at least qualitatively explained within the framework of the Hartree-Fock approximation (including the periodic table and the successes of molecular orbital theory), and thus it is a surprise that density functional  $\mu$  cannot be obtained uniquely at this level of approximation.  $\chi_{\text{spec}}$  contrasts sharply in that almost all of the useful chemical information is obtained at the Hartree-Fock level for most molecules.<sup>4,5</sup> Likewise, in Pearson's Commentary referred to previously, he has pointed out that  $\mu$  does not give reliable estimates of bond polarity nor conform to Pauling's description of electronegativity.<sup>12</sup>

In conclusion, it seems obvious that the electronic chemical potential,  $\mu$ , as developed and applied by Parr, Pearson, et al., is an entirely different chemical quantity than the concept of electronegativity,  $\chi$ , which chemists and physicists have consistently associated with bond polarity. Thus, it creates unnecessary confusion to equate  $\chi$  with  $-\mu$ . For a very long time, electronegativity has been regarded by many scientists as a somewhat "fuzzy" and ill-defined idea, and misappropriation of the word electronegativity would be an unfortunate setback just as a more precise and broadly applicable formulation is beginning to emerge.

(12) In a *Coord. Chem. Rev.* article (in press), Pearson states in regard to his and Parr's identification of  $\mu$  with  $-\chi$ , "But this is a new electronegativity that has been created. It no longer applies to atoms in a molecule so much, but to the entire molecule, radical or ion. Perhaps the word electronegativity should not have been preempted, and the term electronic chemical potential used instead."

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## ARTICLES

### Mechanistic Studies of Light-Induced Charge Separation at Semiconductor/Liquid Interfaces<sup>†</sup>

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The energy crisis of the early 1970s stimulated numerous investigations of semiconductor/liquid junctions for the conversion and storage of solar energy.<sup>1-3</sup> Al-

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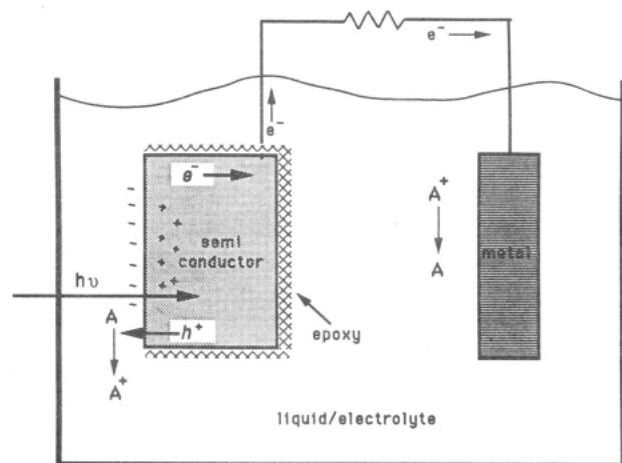
though similar in concept to solid-state photovoltaic devices, semiconductor/liquid junctions offered the potential for inexpensive, chemically based energy-conversion devices, with the accompanying potential to effect the direct conversion of light into chemical fuels.

<sup>†</sup>Contribution No. 8056.

(1) *Semiconductor Liquid-Junction Solar Cells*; Heller, A., Ed.; Electrochemical Society: Princeton, NJ, 1977.

(2) *Semiconductor Electrodes*; Finklea, H. O., Ed.; Elsevier: Amsterdam, 1988.

(3) Rajeshwar, K. *J. Appl. Electrochem.* **1985**, *15*, 1.



**Figure 1.** Schematic of a semiconductor/liquid photoelectrochemical cell. Illumination of the semiconductor with light above its band-gap energy results in the creation of excited mobile electrons and holes in the solid. The electric field at the solid/liquid interface promotes the spatial separation of these charges, producing a faradaic current flow in the cell. The orientation of the field in an efficient cell always drives majority carriers into the bulk of the semiconductor and minority carriers to the solid/liquid interface. In this example, in the absence of illumination, the semiconductor had an excess of electrons (i.e., doped to be n-type), so photogenerated holes are driven to the semiconductor/liquid interface, as indicated by the direction of current flow in the cell. The electrical circuit is completed by motion of the redox ions in the liquid phase from the semiconductor photoelectrode to the metal counter electrode.

The actual photoelectrochemical process is extremely simple: mobile charges are created when a semiconductor electrode absorbs light, and some of these charges are then transferred to ions in the electrolyte solution. This separation and transfer of charge results in production of a photocurrent through the external circuit of the cell (Figure 1).

The apparent simplicity of the process belies the variety of problems encountered in the actual construction of a useful, operating photoelectrochemical device. Earlier investigations of semiconductor/liquid junction photocells in the 1950s and 1960s, by esteemed investigators such as Boddy,<sup>4</sup> Brattain,<sup>5</sup> Gerischer,<sup>6</sup> Morrison,<sup>7</sup> and Memming,<sup>8</sup> had identified a key impediment to utilization and study of these systems in the laboratory: light-induced corrosion of the semiconductor electrode. Later, in the 1970s, renewed efforts were directed at these systems, and many combinations of semiconductors and liquids were discovered that could effect the stable conversion of light into electricity or chemical fuels. During this period, the studies of Heller and Miller,<sup>9</sup> Wrighton,<sup>10</sup> Gerischer,<sup>11</sup> Tributsch,<sup>12</sup> Bard,<sup>13</sup> Parkinson,<sup>14</sup> Fujishima and Honda,<sup>15</sup> and oth-

ers<sup>1-3</sup> revealed many of the principles of semiconductor/liquid junction operation. These studies also identified a few notable systems<sup>16-18</sup> that were highly efficient in the conversion of sunlight into electricity.

A striking generalization of the progress made during this period is that all of the efficient semiconductor/liquid cells had been constructed in contact with aqueous solutions. Furthermore, these cells had all utilized strongly adsorbing inner-sphere redox reagents to stabilize the semiconductor electrode and prevent photocorrosion reactions. During this period, stable cells were also obtained in nonaqueous solvents with outer-sphere redox reagents, but the photovoltaic efficiencies of these systems were generally factors of 10 lower than those of the best aqueous cells.<sup>19-21</sup> This poor electrical behavior was generally attributed to the presence of deleterious electrical recombination sites at the semiconductor/liquid interface.<sup>22</sup> Thus, a paradox was at hand: interfaces that were generally very stable, and suitable for systematic chemical studies, did not provide efficient photovoltaic devices, whereas devices that were generally unstable (aqueous systems) could only be coaxed to exhibit stable, high-efficiency photovoltaic performance with an unpredictable and limited set of inner-sphere redox couples.

The initial goal of our work in this field was to study the behavior of stable semiconductors in nonaqueous solvents, and to elucidate the principles of photoelectrochemical operation using this series of well-defined chemical systems. Questions to be asked include the following: When the photogenerated electron-hole pairs recombine, why do they do so? Where is the recombination occurring: at the solid/liquid interface, in the solution, or in the solid? What is the rate law for charge recombination, and how can we use this information to understand device behavior and to design more efficient systems? The goal of research described in this Account is therefore to understand, from a mechanistic point of view, the fundamental principles that govern the behavior of the semiconductor/liquid junction.

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### Output Characteristics of Photoelectrochemical Cells

The key physical property of a semiconductor/liquid interface is the presence of an electric field at the junction between the two phases. This electric field will generally drive majority carriers (electrons for an n-type semiconductor) into the bulk of the semiconductor and minority carriers toward the surface, leading to the measured charge-separation characteristics of the cell. The form of the electric field has been described in detail in prior work<sup>1-3,23</sup> and in a previous Account;<sup>9b</sup> all that is necessary for our discussion is to realize that the field will rapidly attract photogenerated minority carriers to the solid/liquid interface (Figure 1). This sustained charge-separation process is ultimately responsible for the photocurrents, photovoltages, and power characteristics of interest in photoelectrochemistry.

For a given semiconductor/liquid junction, there are three important electrical output quantities that we wish to understand. The first is the short-circuit photocurrent density,  $J_{sc}$ . This quantity is the current density obtained when the photogenerated charges are free to flow through the external circuit.  $J_{sc}$  provides information on the net quantum yield for charge separation and also serves as a measure of the yield of minority carriers that survive to cross the solid/liquid interface. Note that no net power is produced by the cell at short circuit, because the photogenerated majority carriers do not produce any work as they flow through the external circuit under short-circuit conditions.

The second parameter is the open-circuit voltage,  $V_{oc}$ . This reflects the maximum Gibbs free energy that can be produced by the photogenerated carriers.  $V_{oc}$  is generally measured with a high-impedance voltmeter that is placed between the photoelectrode (the semiconductor) and a metal electrode that senses the electrochemical potential of the electrolyte of interest. No current flows at open circuit, so no net power is produced during this measurement.

The third key output quantity is called the "fill factor". In combination with  $J_{sc}$  and  $V_{oc}$ , the fill factor provides a complete quantitative measurement of the cell's power characteristics. For most photoelectrochemical cells, there are several combinations of current and voltage that result in net power generation through the external circuit. For a particular cell, the maximum  $VJ$  product, divided by  $V_{oc}J_{sc}$ , is defined as the fill factor. The fill factor reflects the ability of the photogenerated current to perform work through an external load and is therefore very sensitive to the kinetics of current flow through the semiconductor/liquid interface.

All of these three parameters,  $V_{oc}$ ,  $J_{sc}$ , and the fill factor, are dependent on the light intensity striking the semiconductor electrode. For a given set of conditions (semiconductor, light intensity, cell temperature, etc.), the fabrication of an efficient photoelectrochemical device involves simultaneous optimization of these three quantities. They are also the primary observables that can be used to obtain mechanistic information regarding the charge-separation and charge-recombination processes in photoelectrochemical solar cells.

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### Short-Circuit Photocurrent

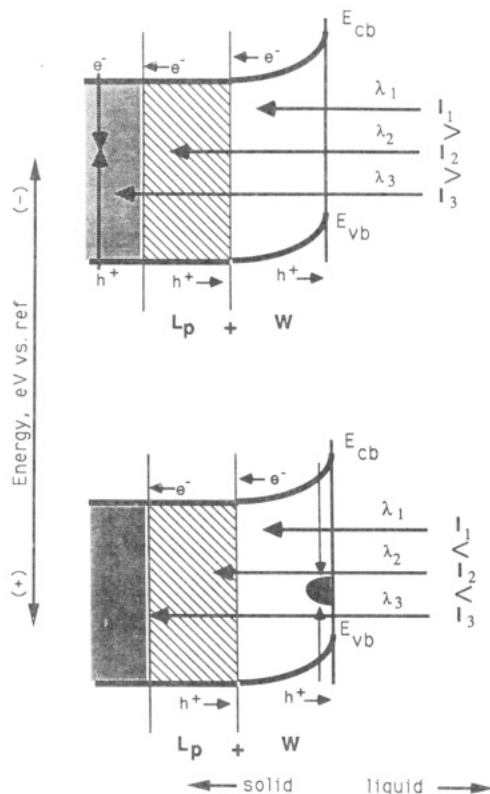
Our first set of mechanistic investigations concentrated on the short-circuit quantum yield, which is reflected experimentally by the value of  $J_{sc}$ . Earlier studies of the behavior of Si,<sup>19a</sup> GaAs,<sup>19b,20a</sup> InP, and other semiconductors in contact with nonaqueous solvents found relatively low short-circuit quantum yields.<sup>2</sup> These low  $J_{sc}$  values were generally assigned to the presence of high surface recombination rates at the solid/liquid junction. To our surprise, in 1981, Chris Gronet, an undergraduate at Stanford University, and I discovered that some samples of n-GaAs in contact with  $\text{CH}_3\text{CN}$ -0.1 M ferrocene (Fc)-0.1 mM  $\text{Fc}^+$ -0.1 M  $[\text{n-Bu}_4\text{N}^+][\text{ClO}_4^-]$  solutions displayed extremely high quantum yields ( $\geq 0.7$ ) when illuminated with 632.8-nm light from a He/Ne laser.<sup>24</sup> Other samples of n-GaAs, with different dopant densities, exhibited lower quantum yields ( $< 0.2$ ) which were in accord with prior literature values, while still others displayed quantum yields approaching 1.0 (based on photons absorbed by the semiconductor). The observation of high quantum yields indicated that rapid surface recombination processes were not present at these particular junctions and that it was possible, for as yet unknown reasons, to efficiently collect the photogenerated carriers from this nonaqueous liquid/semiconductor interface.

We decided to investigate quantitatively the reasons for the variation in recombination among the various n-GaAs samples. Light was a very convenient tool for this study, because the different wavelengths of light have varying penetration depths before being completely absorbed by the semiconductor. Qualitatively, reference to Figure 2 illustrates the situation. If recombination in the bulk semiconductor were the dominant loss mechanism, carriers created by absorption of long-wavelength light should be located so far from the interface that recombination will occur before the carriers can be collected at the solid/liquid junction. This scenario should result in a smaller quantum yield for long-wavelength light than that observed for excitation with more strongly absorbed, shorter-wavelength photons. Alternatively, if surface recombination were the dominant process, then for a fixed photon flux, confining the photogenerated carriers to the surface region should produce an increase in the amount of recombination. This latter situation should produce lower quantum yields with short-wavelength light relative to those found for long-wavelength excitation. Heller et al. had previously used a similar method to qualitatively illustrate the changes in  $J_{sc}$  that could result from etching semiconductor surfaces to be used in aqueous media.<sup>25</sup> We used this method to determine whether the variation in  $J_{sc}$  of the n-GaAs/ $\text{CH}_3\text{CN}$  system was due to a change in surface properties of the various samples or due to a change in the bulk collection properties of these electrodes.

We found that, in all the GaAs samples available to us, the variation in  $J_{sc}$  was completely explained by decreases in the quantum yield for long-wavelength, deeply penetrating photons.<sup>24</sup> This clearly showed that the dominant short-circuit recombination path in the low- $J_{sc}$  samples was in the bulk of the semiconductor,

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**Figure 2.** Use of light as a probe to distinguish bulk recombination processes from surface recombination processes. Consider monochromatic illumination of the semiconductor with three different wavelengths of light,  $\lambda_i$ , where the absorption depths,  $\alpha^{-1}(\lambda)$ , are  $\alpha^{-1}(\lambda_1) < \alpha^{-1}(\lambda_2) < \alpha^{-1}(\lambda_3)$ . If only bulk recombination processes are important, then the quantum yield  $\Phi$  should increase in the order  $\Phi(\lambda_3) < \Phi(\lambda_2) < \Phi(\lambda_1)$ , as a higher fraction of the photogenerated carriers are created within a distance  $L_p + W$  of the interface (where  $L_p$  is the diffusion length and  $W$  is the width of the electric field region). Alternatively, if surface recombination is dominant, then at constant light intensity, the bimolecular rate law for surface recombination predicts that quantum yields will increase in the order  $\Phi(\lambda_1) < \Phi(\lambda_2) < \Phi(\lambda_3)$ .

as opposed to being located at the semiconductor/liquid interface. Furthermore, using a straightforward model of the quantum yield vs wavelength spectral response, advanced in 1959 by Gartner,<sup>26</sup> it was possible to fit quantitatively all of the n-GaAs photocurrent spectra.<sup>24</sup> The only adjustable parameter in the data analysis was the minority carrier collection length, and the values obtained from the spectral response model were later validated with an electron beam induced current collection technique.<sup>27</sup>

Applying this model, it became clear that values of  $J_{sc}$  could be predicted for operating n-GaAs photoelectrochemical cells, provided that one parameter, the minority carrier collection length, was known. This observation was especially significant because it indicated that photoelectrochemical cells with extremely high short-circuit photocurrent densities could be obtained at will, provided that high-quality bulk semiconductor samples were used in the solid/liquid cell.

Further tests of this model were then applied to other semiconductors in nonaqueous solvents. We found that the  $J_{sc}$  values for n-Si,<sup>28</sup> p-Si,<sup>29</sup> n-InP,<sup>30</sup> and other sem-

iconductors<sup>31</sup> could be fit quantitatively in a variety of nonaqueous solvents. Amorphous Si:H alloys were predicted to exhibit a wavelength-dependent fill factor and a power dependence of  $J_{sc}$ , and a-Si:H/CH<sub>3</sub>OH junctions were found experimentally to obey these predictions.<sup>32</sup> The spectral response method has also found use in studying the "back-reaction" of photogenerated majority carriers that are created very close to the semiconductor/liquid interface.<sup>31</sup> To date, it appears that high short-circuit quantum yields can be obtained in the general case, and we are not aware of any semiconductor/liquid junction in nonaqueous solvents whose  $J_{sc}$  values cannot be predicted on the basis of only an application of the Gartner model for the short-circuit photocurrent density.

### Fill Factor

The fill factor was the second observable to draw our attention. The optimization of photoelectrochemical cell efficiency required not only high  $J_{sc}$  values but also high values of the fill factor. Previous studies of Si and GaAs in nonaqueous solvents had revealed low fill factors at solar light intensities,<sup>19,20</sup> which were ascribed to surface recombination processes that were dependent on the applied potential and the light intensity. Only at very high applied voltages, where the power production of the junctions was minimal, could charge be efficiently separated and collected at solar light intensities.

A major breakthrough in our understanding of the behavior of these systems resulted from the improvement of the fill factor of the n-Si/CH<sub>3</sub>OH interface. Professor James Gibbons of the Stanford Electronics Laboratory suggested that the current-voltage behavior of the n-GaAs/CH<sub>3</sub>CN and n-Si/C<sub>2</sub>H<sub>5</sub>OH cells that had been operating in our lab resembled that of a solid-state photovoltaic cell with a high series resistance. Although we initially rejected this idea because the photoelectrodes were under three-electrode potentiostatic control, as described in the literature, further study revealed that the uncompensated ohmic resistance between the working and reference electrodes was very high in certain nonaqueous solvents, especially with relatively low concentrations of electrolyte. Use of the more conducting CH<sub>3</sub>OH-1.0 M LiClO<sub>4</sub> electrolyte, combined with a Luggin capillary, was found to minimize the uncompensated cell resistance. Implementing these changes resulted in a drastic improvement in the fill factor of the n-Si/alcohol interface and demonstrated that surface recombination losses were not the source of the low fill factors for these systems.<sup>33</sup> Combined with the improved  $J_{sc}$  values obtained by use of high-purity bulk n-Si with long minority carrier diffusion lengths, the photoelectrochemical energy conversion efficiency of Si/liquid junctions was increased by over an order of magnitude, from less than 1% to greater than 10% under Air Mass 1.5 conditions.<sup>33</sup> This improvement was notable because it brought Si-based

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photoelectrochemical cells into a range of energy conversion efficiencies that was competitive with Si-based solid-state photovoltaics.

The use of high-conductivity electrolytes to minimize solution resistance was subsequently found to be a key step in improvements of the fill factor of n-GaAs/CH<sub>3</sub>CN,<sup>24,34</sup> p-Si/CH<sub>3</sub>CN,<sup>29</sup> n-InP/CH<sub>3</sub>OH,<sup>30</sup> and a-Si:H/CH<sub>3</sub>OH<sup>32</sup> junctions. The wide variety of semiconductor junctions and redox couples that suffered from this problem illustrates the generality of both the problem and the solution. The importance of uncompensated ohmic resistance can also be seen by visual inspection of the difference in fill factors between high-conductivity aqueous media and low-conductivity nonaqueous solvents for a variety of semiconductor photoelectrodes.<sup>35</sup> To insure that the potentiostatic three-electrode measurements were accurate predictors of photovoltaic performance, a two-electrode thin-layer cell was constructed to minimize the ohmic resistance losses for the n-Si/CH<sub>3</sub>OH system, and extremely high fill factors were obtained, as would be expected in this cell configuration.<sup>36</sup>

### Open Circuit Voltage

**Comparisons between Liquids and Metals.** The remaining observable to be addressed was  $V_{oc}$ . For the n-Si/CH<sub>3</sub>OH system, we observed that variation of the redox potential with a series of outer-sphere redox systems (metallocenes and viologens) led to a change in  $V_{oc}$  of the n-Si/CH<sub>3</sub>OH interface (at constant light intensity, temperature, etc.).<sup>37</sup> This behavior contrasted with the known characteristics of semiconductor/metal junctions based on n-Si, because the semiconductor/metal systems only displayed open-circuit voltages of 0.3 V at  $J_{sc}$  values of 20 mA/cm<sup>2</sup> (and  $T = 300$  K) for a wide variety of metals.<sup>37,38</sup>

For n-Si/metal junctions, the insensitivity of the device properties to the nature of the contacting phase, termed "Fermi level pinning",<sup>38</sup> signaled doom for predictive control of their photovoltaic behavior. On the basis of these results, similar Fermi level pinning behavior had been predicted for Si-based semiconductor/liquid junctions.<sup>22</sup> However, the observed variation in  $V_{oc}$  of Si/CH<sub>3</sub>OH junctions, as expected from a simple, ideal model of the solid/liquid interface, clearly illustrated the differences in junction properties between liquid and metal contacts.<sup>28,37</sup> Improved  $V_{oc}$  values were obtained with the liquid systems, and control over  $V_{oc}$  could be gained by deliberate changes in the composition of the solution phase.

The comparison between liquid and metal contacts was further enhanced by studies of the behavior of p-Si/CH<sub>3</sub>OH and p-Si/CH<sub>3</sub>CN systems, because most metals form either ohmic contacts or poorly rectifying, low- $V_{oc}$  (<100 mV) contacts to p-Si.<sup>38</sup> However, p-Si/CH<sub>3</sub>OH junctions showed  $V_{oc}$  values ranging from 0 to 550 mV.<sup>37</sup> As expected from an ideal junction model, this behavior allowed the construction of high-

efficiency photoelectrochemical cells with p-Si/CH<sub>3</sub>CN-cobaltocene interfaces,<sup>29</sup> despite the prediction that such devices should not display high  $V_{oc}$  values if the Fermi level pinning behavior of semiconductor/metal Si devices were also present for solid/liquid contacts. Similar large- $V_{oc}$  behavior has been observed recently by Mike Heben and Amit Kumar for n-InP/CH<sub>3</sub>OH junctions,<sup>30</sup> and this is consistent with the earlier studies of aqueous p-InP and p-Si/liquid junctions performed in the strongly adsorbing  $V^{3+/2+}$ -6 M HCl electrolyte.<sup>18b</sup>

**Upper Bounds on the Value of  $V_{oc}$ : A Quantitative Mechanistic Approach.** Despite the ability to vary  $V_{oc}$  systematically with a change in redox potential, a remaining mystery was the upper bound on  $V_{oc}$  observed with the semiconductor/liquid junctions. For n-Si/CH<sub>3</sub>OH interfaces,  $V_{oc}$  reached its highest value in the n-Si/CH<sub>3</sub>OH-Me<sub>2</sub>Fc<sup>+0</sup> cell,<sup>37</sup> but the measured value of 0.5–0.6 V was only one-half of the band-gap energy. Thus, the internal energy of absorbed and thermalized photons in the Si semiconductor was 1.12 eV, yet maximum voltage values of only 0.5–0.6 V could be obtained as output in the external electrical circuit. Many qualitative theories in the literature indicated that optimal values of  $V_{oc}$  should approach  $E_g/q$ <sup>39–41</sup> (with  $E_g$  the band-gap energy in eV), but no quantitative data were available to confirm these hypotheses.  $V_{oc}$  values significantly lower than  $E_g/q$  were interpreted as signaling wasted energy and were thought to result from restrictions on the photovoltage due to surface states that pinned the position of the semiconductor surface Fermi level.<sup>22</sup> It was hypothesized that these states made it impossible to reach the optimal  $V_{oc}$  values of approximately  $E_g/q$ .

Using the n-Si/CH<sub>3</sub>OH system, Mary Rosenbluth decided to test this hypothesis by performing kinetic studies on the semiconductor/liquid interface. Based on the extensive literature of solid-state photovoltaics,<sup>38,42</sup> we realized that  $V_{oc}$  was a light intensity dependent quantity and was a property of a particular photostationary state. Therefore,  $V_{oc}$  could not be related to a thermodynamic property,  $E_g$ , without consideration of the rate constants and external variables that described the specific system under study. We also realized that there were many possibilities for the rate-limiting process, and that a kinetic study would be needed to elucidate the mechanism of carrier recombination. Many of these concepts had been developed in the work of Gerischer and co-workers<sup>43</sup> and by Myamlin and Pleskov<sup>44</sup> during 1955–1965, but had not been applied to mechanistic studies of the subsequently developed stable photoelectrochemical cells.

The mechanistic pathways of interest are depicted in the kinetic scheme of Figure 3.<sup>37,42</sup> Pathways  $J_{th}$  and  $J_{th}$  both depict electrons (majority carriers in this n-type

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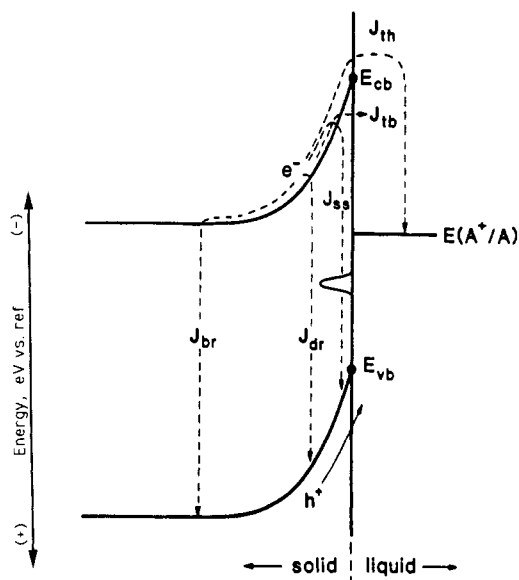
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**Figure 3.** Schematic illustration of the various different recombination pathways possible at semiconductor/liquid interfaces.  $J_{th}$  represents majority carrier electron transfer to solution acceptor ions ( $A^+$ ), while  $J_{tb}$  represents the same process accompanied by partial tunneling through the electric potential barrier in the depletion layer. Pathways  $J_{ss}$ ,  $J_{dr}$ , and  $J_{br}$  represent surface-state recombination, depletion-region recombination, and bulk-region recombination, respectively. Each pathway can be diagnosed by its distinctive functional form on the various values of the depletion width, applied voltage, photocurrent density, and cell temperature.

semiconductor example) going “the wrong way”, i.e., crossing the interface, as opposed to being driven into the bulk and through the external circuit. Process  $J_{th}$  involves electrons being thermally activated over the entire electric potential in the semiconductor space charge region and then crossing the interface by capture with a solution-based acceptor species. Process  $J_{tb}$  is similar, except that the electron tunnels through some portion of the electric potential barrier and then proceeds into an acceptor state in solution. The other three processes all involve recombination of a minority carrier with a majority carrier and are distinguished by where this recombination takes place in the solid. Process  $J_{ss}$  refers to surface-state recombination, process  $J_{dr}$  refers to recombination in the space charge region, and process  $J_{br}$  refers to recombination in the bulk, or quasi-neutral, region of the semiconductor.

This kinetic scheme is very useful for elucidating the properties of a given semiconductor/liquid interface. All of the rates depicted in Figure 3 proceed in parallel; thus, the magnitude of each kinetic process must be summed in order to obtain a value for the overall recombination rate. Furthermore, if we know the rate-limiting step, its rate can be expressed as a recombination current density, and we can then use a simple, well-known expression<sup>38,42</sup> to predict the resulting  $V_{oc}$ :

$$V_{oc} = (kT/q) \ln (J_L/J_0) \quad (1)$$

Here,  $J_L$  is the light-generated photocurrent density and  $J_0$  is the recombination current density at zero applied voltage to the semiconductor/liquid interface.

For the n-Si/CH<sub>3</sub>OH–Me<sub>2</sub>Fc<sup>+0</sup> junction, kinetic studies were used to prove that the  $J_0$  in eq 1 corresponded precisely to that expected for the rate process  $J_{br}$ . Variation in dopant density, minority carrier diffusion length, photocurrent density, and cell tempera-

ture all yielded changes in  $V_{oc}$  as predicted by eq 1 and the expected variation in  $J_{br}$ .<sup>28,42,45</sup> This study provided kinetic proof that the rate-determining recombination step in the n-Si/CH<sub>3</sub>OH–Me<sub>2</sub>Fc<sup>+0</sup> junction did not directly reflect the junction kinetics, but was limited by the value of recombination in the bulk of the solid. It also formed a basis for the prediction of  $V_{oc}$  by knowledge of the rate-determining recombination step for the junction of interest. Minimizing the factors affecting  $J_0$  led to a 670-mV  $V_{oc}$  at  $J_{sc} = 20$  mA/cm<sup>2</sup>,  $T = 300$  K for the n-Si/CH<sub>3</sub>OH–Me<sub>2</sub>Fc<sup>+0</sup> interface.<sup>28</sup> This understanding provided the basis for construction of a 14% efficient photovoltaic cell based on the n-Si/CH<sub>3</sub>OH junction.<sup>36</sup>

Notably, the fact that the rate-determining recombination step is in the bulk semiconductor means that no junction formed with this specific sample of n-Si could have a  $V_{oc}$  larger than that observed for the n-Si/CH<sub>3</sub>OH interface. An equivalent statement is that  $J_0$  is already at its minimum value for this particular sample. This comparison is particularly significant with regard to solid-state p–n photovoltaic systems, because it implies that the  $V_{oc}$  obtainable with the solid/liquid junction will be greater than or equal to the  $V_{oc}$  for a solid-state system made with the identical Si material. Furthermore, the relative efficiency of the two different types of systems will then only be affected by the relative improvements in processing (to minimize light reflectivity, series resistance, contact resistance, and contact recombination, etc.) of the photovoltaic devices. The 14% efficient Si/liquid junction cell is one of the most efficient semiconductor/liquid junctions known to date, and its efficiency also compares favorably to the 10–15% solar efficiencies typically obtained from solid-state p–n junction photovoltaics made with similar quality Si.<sup>42</sup>

Additionally, it can be noted that none of the recombination rates depicted in Figure 3 depend in the same fashion on the four variables of dopant density, minority carrier diffusion length, photocurrent density, and cell temperature.<sup>37,42</sup> Quantitative studies of the dependence of  $V_{oc}$  on these fundamental variables can, in principle, yield kinetic information on the rate-determining recombination step for any semiconductor/liquid system. This methodology has recently been applied to p-InP/CH<sub>3</sub>CN,<sup>46</sup> n-InP/CH<sub>3</sub>OH,<sup>30</sup> and n-GaAs/CH<sub>3</sub>CN<sup>34</sup> interfaces and should find application in most photoelectrochemical devices of interest. Obviously, if one understands the functional form of the variables that control  $V_{oc}$ , it will be relatively easy to make predictive variations in these quantities in order to obtain larger photovoltages and more efficient photoelectrochemical devices.

### Minority Carrier Characteristics: Effects of Surface-State Passivation vs Electrocatalysis

The kinetic discussion to this point has focused primarily on the recombination properties of the majority carriers inside the semiconductor. However, the interfacial kinetics of minority carriers can also be important in determining the photovoltaic characteristics of semiconductor interfaces. For minority carriers to

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cross the interface and produce a photocurrent, recombination with majority carriers must be suppressed. A particularly facile kinetic pathway that can produce a loss of minority carriers is surface-state recombination (process  $J_{ss}$  in Figure 3). If surface-state recombination is important, then it might be expected that chemical reagents that reduce the number of surface states, or that reduce their rate constants for charge capture, would be effective in improving the photoelectrochemical characteristics of semiconductor surfaces. The solid/liquid junction is an excellent system to correlate the chemical and electrical properties of a surface treatment, because the nature of the surface bonding and the resulting electrical properties can be obtained simultaneously for the interface of interest.

The pioneering work in this area was performed in 1977 by Parkinson, Heller, and Miller,<sup>16</sup> who showed that chemisorption of  $Ru^{3+}$  ions onto n-GaAs photoanodes produced substantial improvements in the photovoltaic properties of the n-GaAs/KOH- $Se^{-/2-}$ /C cell. Some other aqueous solutions of common transition-metal ions were also noted to improve the I-V properties of the n-GaAs surface,<sup>16</sup> but  $Ru^{3+}$  was the most effective ion studied. The observation that chemisorption of ions could modify, and improve, the electrical behavior of a semiconductor junction is a significant and encouraging finding for all future studies of the interfacial chemistry of semiconductor junctions.

As of 1987, both the chemistry of  $Ru^{3+}$  chemisorption on GaAs and the mechanism of  $Ru^{3+}$  I-V improvement of the n-GaAs/KOH- $Se^{-/2-}$ /C cell were unknown. The mechanistic concerns focus on whether the improved photovoltaic properties resulted from a decreased surface recombination rate or from an increased rate of minority carrier capture by the electrolyte. Using this solid/liquid junction as a model system, Ian Abrahams, Bruce Tufts, and I developed a protocol for separating these two pathways and for analyzing the effects of surface treatments on minority carrier kinetics.

The key experiments were performed on p-GaAs/KOH- $Se^{-/2-}$  junctions.<sup>27,47,48</sup> At an illuminated n-type semiconductor/liquid interface, holes are the minority carriers, and the ratio of the interfacial crossing rate to the surface-state recombination rate will determine the net quantum yield for photocurrent production (Figure 3). In contrast, for a p-type semiconductor, holes are majority carriers, and the hole current is the sum of the interfacial crossing rate and the surface-state recombination rate. Thus, if the role of  $Ru^{3+}$  ions is to reduce the hole surface recombination rate, the observed majority carrier (hole) current should be reduced (at a given voltage) for  $Ru^{3+}$ -treated p-GaAs/KOH- $Se^{-/2-}$  junctions relative to that for untreated p-GaAs surfaces. However, if the chemisorbed ions act to increase the hole charge-transfer rate, the observed current for p-GaAs should be larger after  $Ru^{3+}$  chemisorption. The comparison of p-GaAs with n-GaAs in the same electrolyte also ensures that similar surface chemistry, adsorption characteristics, and electrolyte effects are maintained, because these characteristics should be relatively insensitive to the small change in

composition from <1 ppm Te dopant in n-GaAs material to <1 ppm Zn dopant in p-GaAs material.

The studies of p-GaAs revealed that chemisorption of  $Ru^{3+}$  increased the dark currents at a given voltage.<sup>27,47</sup> This result implied that the predominant kinetic role of  $Ru^{3+}$  chemisorption was to increase the interfacial hole capture rate constant in the KOH- $Se^{-/2-}$  cell. This conclusion was also supported by studies of polycrystalline n-GaAs anodes in KOH- $Se^{-/2-}$  media performed by Sharon Lunt,<sup>49</sup> by studies on  $In_2O_3$ /KOH- $Se^{-/2-}$  junctions,<sup>27</sup> by studies of  $n^+$ -GaAs/KOH- $Se^{-/2-}$  cells,<sup>27</sup> and by real time luminescence studies of GaAs/KOH- $Se^{-/2-}$  interfaces performed by Gail Ryba and Pat Santangelo.<sup>50</sup> Additionally, the result predicts that ions that yield increased hole-transfer rates in KOH- $Se^{-/2-}$  electrolytes should effect improved photovoltaic efficiencies at n-GaAs anodes. A series of n-GaAs surface modifications has been investigated based on group VIIIIB metal complexes, and the predicted trend in efficiency has been verified experimentally.<sup>27,48</sup> Additionally, this correlation has led to the use of chemisorbed  $Os^{3+}$  on n-GaAs to produce a 16% efficient photoelectrochemical cell from n-GaAs/KOH- $Se^{-/2-}$  junctions.<sup>47</sup> This is currently the highest reported efficiency for any photoelectrochemical cell under solar illumination conditions, and it was achieved through a mechanistic understanding of the important interfacial charge transfer rates.

This approach should be quite general in determining whether improvements in the I-V properties after surface modification are due to a reduction in the rate of minority carrier recombination or to an increase in the rate of minority carrier collection across the solid/liquid interface. Surfaces where this technique might be applied include p-InP/Ag<sup>+</sup>,<sup>51</sup> n-CdS/ $Ru^{3+}$ ,<sup>52</sup> n-CdSe/amines,<sup>53</sup> and n-PdPS/ $Fe(CN)_6^{3-/4-}$ ,<sup>54</sup> all of which have displayed improvements in photovoltaic output properties as a result of deliberate surface-modification procedures. This phenomenon also points out a difference between semiconductor/liquid and semiconductor/metal junctions, because in the latter, the density of states in a metal is sufficiently large that all minority carriers that reach the semiconductor/metal interface are rapidly captured. Thus, for metal contacts, no change in I-V properties should occur even after chemisorption of species that increase the minority carrier injection rate into a specific electrolyte. Indeed, this was found to be the case for the n-GaAs/M contacts where M = Au and the ions were  $Ru^{3+}$  and  $Co^{3+}$ .<sup>27,48</sup>

To date, the chemistry of electrical traps on the GaAs surface has not been elucidated, because no species has yet been found that improves the photoelectrochemical I-V characteristics by decreasing surface-state recom-

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bination as opposed to improving the minority carrier capture kinetics. This is an active area of investigation and presents a challenge for scientists involved in the chemistry of interfaces.

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## Semiconductor Crystallites: A Class of Large Molecules

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### Introduction

Silicon, gallium arsenide, and cadmium selenide, are examples of semiconductors, a class of materials indispensable to modern solid-state electronics. Their properties can be understood in molecular terms. The Si-Si bond in bulk silicon is localized, tetrahedrally directed, and strong and, in fact, is no different than that in organosilicon molecular compounds. The relationship between bulk silicon and the silicon atom is similar to the relationship between organic polymers and their constituent monomers. A piece of bulk silicon is simply a normal, albeit extremely large, inorganic molecule.

Semiconductor electronic properties are a consequence of the molecular orbitals of the solid. Consider a small silicon crystallite growing from Si atoms, as schematically outlined in Figure 1.<sup>1-4</sup> The atom has four sp hybrid orbitals. Orbitals on neighboring atoms combine pairwise to form doubly occupied bonding orbitals and empty antibonding orbitals. Each new atom adds one orbital to the bonding set and to the antibonding set, for each bond formed. A spread of orbital energies develops within each orbital set, and the HUMO-LUMO separation in the molecule becomes the band gap of the solid.

Semiconductor electronic properties depend strongly on the extent and dimensionality of polymerization, that is, on the size and shape of the oligomer. Only one dimension need become macroscopic for the bands to become continuous. Very thin sheets (termed "quantum wells" in the physics literature) show bulk solid-state properties in the two planar dimensions, but molecular, size-dependent properties in the thin dimension.<sup>5</sup> The interplay of solid-state and molecular properties in such structurally perfect, layered materials has led to remarkable discoveries: the fractional quantum Hall effect, ballistic electron transport, and

large nonlinear optical effects.

In 1983 we began studying the *three-dimensional* evolution of molecular to bulk properties in large semiconductor clusters (alternative terms: quantum crystallites or quantum dots).<sup>6</sup> These large structures have the internal geometry of the bulk solid, but electronic properties similar to those of molecules. We attempt to invent methods to synthesize, characterize, and understand *macroscopic amounts* of large (100-5000 heavy atom), chemically passivated clusters. We study large clusters because we find that bulk electronic properties develop slowly with size. The study of these clusters is a new branch of the chemistry of large molecules.

### Preparation and Characterization of Large Semiconductor Clusters

**Molecular Synthesis of Large Clusters.** An ideal synthesis would prepare *pure* isolated clusters, monodisperse at the atomic level, with the surface independently derivatized. Cluster size would be continuously variable, and a wide class of surface ligands would be possible, to impart desired surface properties. The enormity of this project is obvious, yet an encouraging start has been made.

Most progress has occurred with II-VI binary compounds. These semiconductors have small solubility products, ease of internal crystallization, and simple phase diagrams. Crystallinity is essential in the current schemes for internal structural characterization. Simple phase diagrams help ensure that only one type of cluster is formed.

The precipitation of sulfides and selenides occurs in textbook qualitative analysis schemes. The process can be stopped kinetically at a size near the smallest homogeneous nucleation seed by working at very high dilution and/or low temperature.<sup>7,8</sup> The resulting

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