MASTER

FLASH PHOTOELECTROCHEMICAL STUDIES OF TRANSIENT
ELECTRODE PROCESSES IMPORTANT IN SOLAR ENERGY CONVERSION

Progress Report
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OVERVIEW

The plan of study in our renewal proposal of December, 1979, related to pulsed laser irradiation of semiconductor/liquid junction photoelectrochemical cells, outlined the following specific areas for progress during 1980: (1) detect and characterize transient photoproducts due to electrode and/or solution photoelectrolysis at the interface; (2) obtain time-resolved photoelectrolysis data indicative of charge transfer rates; (3) obtain photoelectrochemical measurements related to electron-hole recombination rates subsequent to pulsed laser irradiation; (4) utilize complementary spectroscopic methods for characterizing transient photoprocesses at the semiconductor/electrolyte interface; and (5) characterize the dynamics of "super-sensitizer" interactions with sensitizing dyes adsorbed at the interface. Another related area of work in which we have made progress this year, but which was not included in the 1980 plan of study, is (6) direct observation of surface state photoelectrolysis processes.

This Progress Report summarized the accomplishments of this past year. Two points should be emphasized here. Firstly, not only have all of the above goals for 1980 been achieved, but we have also initiated work in one additional related area. Secondly, the results obtained provide for the first time some direct evidence for the very rapid chemical and physical processes occurring at an irradiated semiconductor/electrolyte interface. This past year has clearly marked a turning point in this research program. Whereas prior to 1980 we were very much concerned with the development of methodology and instrumentation to obtain reliable and meaningful photoelectrochemical data in the nanoseconds time domain, the work completed during this past year has focused on extracting useful information about the nature and dynamics of the transient chemical and physical processes initiated by pulsed

laser irradiation of semiconductor/liquid junction solar cells. The results obtained will allow us to initiate the next phase of the research program (detailed in the Renewal Proposal, December, 1980), which involves establishing correlations between the characteristics of transient photoprocesses and the resultant solar energy conversion efficiency and durability of various liquid junction solar devices.

SCOPE OF INVESTIGATIONS

We are particularly concerned with studies of transient phenomena associated with photo-initiated processes at an electrode/electrolyte interface. These processes may be related to oxidation/reduction of excited species, or photoelectrolysis at semiconductor electrodes. During the initial stages of this contract we investigated the effects of various laser sources on photoemission phenomena, and began to look at transient photocurrents generated with flash irradiation of a semiconductor electrode/electrolyte interface. During the second and third years of the project we completed the development of experimental techniques and theory for sub-microsecond time-resolved photoelectrolysis studies, and completed preliminary studies of transient photoinduced processes at metallic and semiconductor electrodes. During this past year we have begun to collect significant data regarding the chemistry and physics of very rapid photo-induced electrode processes at various semiconductor materials, which provide for the first time the direct observation of primary steps in photoelectrochemical solar energy conversion.

The work described here was initiated at Purdue University. However, for those experiments requiring very short laser pulses (≤ 10 nS) the work was conducted in collaboration with Dr. J. H. Richardson at Lawrence Livermore National Laboratory. Thus, items 1, 5, and 6 in the Overview (P. 1) were conducted entirely at Purdue, items 3 and 4 were conducted entirely at LLNL,

while item 2 was pursued cooperatively at both laboratories. Because the equipment and scientific interests of the two laboratories are complementary, this has been a very fruitful collaboration.

RESULTS

(1) Detection of Primary Photoelectrolysis Products.

We have used both cyclic voltammetry (CV) and flash/potential-step experiments to characterize photoelectrolysis products for several different types of semiconductor electrodes and several different solution redox couples. (The flash/potential-step method was developed here and characterized in previous Progress Reports.) The materials studied included n-type electrodes (single crystal TiO_2 and polycrystalline TiO_2 and Fe_2O_3) and a p-type electrode (single crystal GaAs). In addition to oxidation/reduction of water, we also observed the photoredox behavior of Tl^+ (at the n-type electrodes) and of Eu^{3+} and Fe^{3+} at p-GaAs.

For all of these electrodes cyclic voltammetry under continuous irradiation with scan rates up to 20 V./s. did not show any significant reverse current due to detection of water photoelectrolysis products in neutral solution, at high pH (n-type electrodes), or low pH (p-type). When Tl^+ was added to the solutions for n-type electrodes, both anodic and cathodic peaks were observed under irradiation, indicating that the photo-oxidation of Tl^+ occurs at the anodic peak and the cathodic peak is the detection of Tl^{3+} photo-oxidation product. (A similar observation was made for anodic and cathodic currents obtained with flash/potential-step experiments.) The magnitude of the CV peaks were independent of $[\text{Tl}^+]$. When Eu^{3+} or Fe^{3+} were added to neutral solution with p-GaAs, cathodic photoreduction peaks were observed for both, and they were concentration-dependent. A reverse (anodic)

peak was observed for Eu^{3+} , which was also concentration dependent, but no reverse peak was ever observed for Fe^{3+} . The observed reverse peak for Eu^{3+} indicates that the photoreduction to Eu^{2+} occurs during the cathodic scan, and that the Eu^{2+} is detected (re-oxidized) on the reverse scan. At low pH, the addition of Fe^{3+} or Eu^{3+} does not lead to enhanced photoreduction beyond that due to the solvent/electrolyte; and no reverse (anodic) current is observed with cyclic voltammetry. (Of course, no significant redox current is observed at all in the dark within the potential range covered by cyclic voltammetry.)

The insensitivity of irradiated p-type GaAs to EuCl_3 and $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$ in 1 N H_2SO_4 electrolyte is apparently because the high concentration of hydronium ion competes too well for the conduction band electrons. In neutral solution, the exchange orbitals of Eu^{3+} and Eu^{2+} overlap well with the conduction and valence bands, respectively, and the reduction of Eu^{3+} to Eu^{2+} can compete with hydronium ion for conduction band electrons. During the reverse scan Eu^{2+} is oxidized back to Eu^{3+} by valence band holes. A slightly different situation exists for the iron redox couple. Like Eu^{3+} , good overlap between Fe^{3+} and the conduction band exists. However, the exchange orbital for Fe^{2+} is quite low, as is the standard reduction potential (compared to Eu^{2+}), which probably accounts for the significantly lower oxidation current on the reverse scan.

Truly complementary information was obtained from flash photolysis photoreduction of Eu^{3+} and Fe^{3+} at p-type GaAs. The amount of photoreduction current was found to be dependent upon either the Eu^{3+} or Fe^{3+} concentration when the electrode was continuously irradiated. However, no concentration dependence on q_F (the integrated photocurrent pulse) was observed when flash irradiation was used, even at energy levels approaching the energy output of

the continuous lamp. The conclusion, therefore, is that the charge transfer process between GaAs and either Eu^{3+} or Fe^{3+} is too slow to be observed on the time scale of the flash photolysis experiment ($\approx 10 \mu\text{s}$). Accordingly, no reverse (anodic) current was observed with flash/potential-step experiments, in contrast to the results with Tl^+ at TiO_2 .

Because cyclic voltammetry did not detect photoelectrolysis products at any pH for all the electrodes studied, in the absence of added redox couples, we made an effort to detect any short-lived intermediates or photo-products using the flash/potential-step method. Before and during the flash the potential of the electrode was adjusted for favorable photoelectrolysis of water. The potential step was triggered electronically, 25 μs after the initiation of the flash. A q_{NET} was obtained for a series of progressively larger reverse potential steps.

Potential step experiments for n-type electrodes in 1 M NaOH yield a zero q_{NET} . This is consistent with the cyclic voltammetry experiments. However, in 0.1 M Na_2SO_4 q_{NET} is non-zero. To test the presumption that the non-zero q_{NET} is the result of a Faradaic current, a set of experiments were conducted with a constant potential step but variable time delay, τ . By doing this, the initial difference between the current due to a potential step and a potential step after a flash could be measured over a wide range of delay times. The observation made is that the net current detected by a potential step after a flash decays as $1/\sqrt{\tau}$. This result is consistent with the detection of a photoproduct diffusing away from the electrode. This photoproduct was detected in the time domain of 50 μs to 10 mS .

Studies done elsewhere indicate that while TiO_2 is stable in alkaline electrolytes, it is unstable in neutral and acid media. Therefore, because q_{NET} was observed to be non-zero in 0.1 M Na_2SO_4 we attribute this latter

result to electrode dissolution. This is also consistent with the results observed for iron oxide electrodes.

Measurements of q_{NET} for p-type GaAs with flash/potential-step experiments were also consistent with steady state observations on electrode stability. That is, GaAs is observed to be unstable in either neutral or acidic medium; and q_{NET} in either electrolyte is non-zero. Again, this observation is in contrast to the inability to detect a photoproduct with cyclic voltammetry.

To conclude, the results reported above point up the very significant fact that the characteristics of semiconductor photoelectrolysis processes can change dramatically depending on the time domain over which they are observed. Our experiments clearly show that transient photoproducts are detectable. Moreover, our results provide some insight into the dynamics of the charge transfer processes---showing, for example, that Eu^{3+} and Fe^{3+} are not photo-reduced rapidly at GaAs. The detection of transient photoproducts for all of the electrodes studied here, only under conditions where long-term photodissolution occurs, is a singularly interesting fact. For TiO_2 , at least, this product appears not to be bound to the electrode.

Obviously, more work needs to be done. For example, the contrasting results with Eu^{3+} and Fe^{3+} at GaAs for continuous and pulsed irradiation suggest that photoelectrolysis proceeds via a surface intermediate (due to initial photoreduction of GaAs) which then reacts slowly with Eu^{3+} and Fe^{3+} . Thus, it would be informative to extend these studies to non-aqueous solutions which might preclude subsequent redox chemistry and allow in-situ surface analysis as described in the Renewal Proposal.

Another example of a puzzling observation is the inability to detect an intermediate photoproduct under conditions where the electrode is stable.

The inference is that the normal water photoproducts (O_2 , H_2) are not detectable, but the electrode dissolution photoproducts are. However, this conclusion can only be evaluated with complementary spectroscopic data as suggested in our Renewal Proposal.

(2) Measurements of Charge Transfer Rates.

We have made considerable progress over the past year in this area along several fronts. One of these was described in section [1] above, where indirect evidence for relative charge transfer rates was obtained. For example, we demonstrated that Eu^{3+} and Fe^{3+} could not compete favorably with H^+ for photoreduction at GaAs in low pH solutions, but could in neutral solution. Also, we showed more directly that Eu^{3+} and Fe^{3+} were not reduced significantly during a $10\mu s$ pulsed irradiation experiment in neutral solution, while continuous irradiation resulted in significant photoreduction.

An area where we have begun to obtain direct evidence for charge transfer rates is with coulometric-flash experiments, where 10 ns laser pulses have been employed and instrumental rise time is ~ 1 to 15 ns. These studies have been conducted with n- TiO_2 and n-CdS electrodes under a wide variety of solution conditions. Using a pulsed dye laser, we have observed the responses to super-bandgap- and sub-bandgap-energy wavelengths.

For TiO_2 , in alkaline or neutral solutions we observe essentially an instantaneous (~ 10 ns) rise of the "photopotential" to a plateau value. Moreover, when we add a current-doubling reducing agent such as Tiron (4,5-dihydroxy-m-benzene-disulfonic acid), we observe an enhanced photopotential excursion, with the same rise time as without the reducing agent. Thus, we conclude that (a) the potential excursion is indeed due to charge transfer in addition to photo-induced charge separation, and (b) the charge transfer

rate at TiO_2 for water oxidation (and Tiron oxidation) is so fast as to appear instantaneous with a 10 ns light pulse. There had been some concern earlier that the initial potential excursion was due only to charge separation. However, it is clear that the signal would not be enhanced by the presence of a current-doubling agent if it only reflected initial charge separation, as that would depend only on the light intensity which did not vary.

For CdS, in alkaline S^{2-} and S_x^{2-} solutions, and in non-aqueous LiClO_4 solution, we have observed a two-step rise in the photopotential with pulsed laser (visible) irradiation (Figure 1). The first step is complete in ~10-20 ns, whereas the second step requires ~20 to 200 ns. Because this latter step is independent of solution conditions we conclude that the initial charge transfer reaction probably involves production of S/S^- (extrinsic holes) from S^{2-} at the CdS electrode surface. The rapid first step in the photopotential is probably due to initial charge separation in the space charge

Figure 1. Typical CdS transient photopotential response at short times near the band absorption edge: 1 M NaOH and 1 M Na_2S , initial potential = + 0.5 V vs. SCE, 512 nm, laser power = 2.2 kW (~220 kW/cm^2).

layer, while the second step probably reflects the slower subsequent charge transfer process. We have also shown that the rise time of the second step has a well-defined wavelength and intensity dependence. Thus, we have concluded that variation of drift times of charge carriers through the semiconductor depletion layer occurs as a function of laser power and wavelength, which affects the net population of holes at the surface, and thereby affects directly the charge transfer rate.

With pulsed UV irradiation, in the presence of $S_x^{=}$, the single-step rise time was $\sim 1 \mu s$, (Figure 2). The slow response with polysulfide represents

Figure 2. Typical CdS transient photopotential response with polysulfide solution: 1 M NaOH, 1 M Na_2S , and 1 M S, initial potential = 0.0 V vs. SCE, 337 nm, incident laser power = 100 kW ($\sim 2 MW/cm^2$).

the dynamics of the interaction of irradiated solution with the semiconductor electrode. This is clear from the dependence of the temporal response on solution composition, polysulfide concentration, electrode potential and surfactant. This slow response is probably due to light absorption by

polysulfide ions. The apparent correlation between the action spectrum of this slow risetime and the polysulfide absorption spectrum supports this suggestion. Further support is found in the diminishing of the CdS electrode luminescence with the concomitant increase in both the polysulfide concentration and the coulostatic-flash response time. It is unlikely that the initial step is light absorption by the CdS electrode and the production of holes, followed by subsequent chemical and physical interactions. In all other cases we have observed that the photoproduction of holes results in a very fast (~ 10 ns) potential excursion. Thus, in this case it is likely that polysulfide adsorbed on the electrode surface is responsible. The polysulfide could slowly interact with the CdS electrode to produce oxidized polysulfide at the surface. The exact nature of this interaction is not yet completely elucidated (a tunneling-like mechanism may be implicated by the dependence on electrode potential; the barrier depth decreases as the potential is made more positive of flat band). However, it is just that type of interaction, resulting in a slower rate of charge transfer, which would be deleterious to the overall efficiency of any solar energy conversion system. For example, this work demonstrates that there is an optimal polysulfide concentration range with respect to the rate of charge transfer with uv irradiation. It is expected that laser coulostatic-flash experiments will be able to furnish further insight into these processes which appreciably decrease the rate of charge transfer.

One definite conclusion is that, except for the CdS/polysulfide solution with uv irradiation, the initial charge separation step is essentially complete under normal illumination conditions within 10 ns. This step is relatively independent of solution chemistry; consequently, it should ultimately be possible to draw comparisons between this type of work and similar measurements

made at Schottky barriers or electrode-air interfaces. Our current temporal resolution is sufficient for investigating certain anomalous effects with high laser intensities, chemical back reactions, and probably fairly fast redox chemistry subsequent to the initial potential excursion and charge transfer. However, it may be necessary to develop time-resolved spectroscopic techniques to probe the initial steps important in efficient solar energy conversion within the required time scale. Spectroscopic techniques offer the possibility of greater molecular specificity than that attainable with coulstatic techniques. The correlation of data from these two techniques should provide particularly valuable insights into the dynamics of processes at irradiated semiconductor electrode interfaces.

(3) and (4). Measurements of Electron-Hole Recombination Rates. (Photoelectrochemical and Spectroscopic Studies.)

To aid in our interpretation of the coulstatic response at a CdS electrode, we have measured the luminescence lifetime at an irradiated Te-doped CdS electrode in aqueous alkaline sulfide solution under a variety of conditions (e.g., different excitation wavelengths, laser intensities, and electrode potential). The steady-state photoelectrochemical and spectroscopic properties of Te-doped CdS electrodes have been previously reported, and our electrode characterization was consistent with those results. One of the salient conclusions previously derived is the good correlation between the photoelectrochemical properties of the emitting (Te-doped) and non-emitting CdS electrodes. Consequently, our time-resolved luminescence measurements can be correlated to both the steady-state luminescence measurements which use Te-doped CdS and the transient photoelectrochemical measurements which used a less luminescent dopant.

The luminescence lifetimes reported here are consistent with the coulstatic measurements made using CdS electrodes (reported in section [2]. Specifically, in the coulstatic experiment the electrode potential can be driven past the flat-band potential with an intense laser pulse. The maximum negative potential is reached in ≤ 10 ns, but the electrode potential quickly returns to the flat-band potential in ≤ 50 ns (Figure 3). We can now conclude,

Figure 3. Typical CdS transient photopotential response at short times and high laser power; 1 M NaOH and 1 M Na₂S, initial potential = + 0.5 V vs. SCE, 455 nm, laser power = 40 kW (~ 4 mW/cm²).

because of the similarity of the two rates at the same laser intensity (i.e., luminescence decay and potential decay), that this return to the flat band potential is consistent with a mechanism based largely on electron-hole recombination. The rate of electron-hole recombination is reflected by the luminescence decay rate, although the majority of electron-hole recombination events proceeds by a non-radiative mechanism; even with Te-doped CdS the quantum yield for luminescence is less than 1%. Electron-hole recombination

(radiative plus non-radiative decay) is a primary deactivation pathway from the excited state of the semi-conductor; Faradaic processes (electron-hole separation followed by electrode photodissolution or solution oxidation/reduction) generally proceed with less than 50% quantum efficiency. Furthermore the quantum efficiency of Faradaic processes (electron flow/photons absorbed) decreases as the laser power is increased; under these conditions electron-hole recombination is even more important.

The subsequent slow (μs to ms) return of the electrode potential to the cell equilibrium value in the laser coulostatic experiment is due solely to redox chemistry at the interface and possibly to an equilibration of the charge distribution in the depletion layer. On this slower time scale electron-hole recombination is essentially complete and does not play a significant role.

An unusually slow (~ 200 ns) coulstatic response was observed at wavelengths corresponding to band gap (515 nm) illumination. This slow response had a wavelength maximum at 515 nm. It was suggested that this slow coulstatic response was due to excitation deeper in the semiconductor and the subsequent slower separation of electron-hole pairs where the potential gradient was less. The long luminescence lifetime observed here at 515 nm is consistent with this interpretation.

In conclusion, time-resolved luminescence measurements at an illuminated semiconductor electrode provide useful insight into the rates of chemical and physical processes occurring in semiconductor liquid-junction solar cells. This insight may prove particularly valuable if it can be correlated with the information developed in time-resolved photoelectrochemical measurements. With intense laser illumination, even semiconductors containing less luminescent dopants than Te will emit. Consequently this technique should prove of value in characterizing a wide variety of potential semiconductor electrode materials.

(5) and (6). Coulostatic-Flash Studies of Dye-Sensitized Photoelectrolysis and Direct Sub-bandgap Irradiation.

The interest in chemical "sensitizers" for semiconductor photoelectrolysis derives from the fact that the most stable semiconductor electrodes have a large bandgap (e.g., TiO_2 , SrTiO_3 , etc). Thus, the use of an adsorbed dye, a chemically-bonded surface chromophore, or a low-bandgap semiconductor absorber (n-type) bonded to a larger bandgap (p-type) material exposed to solution are various ways of sensitizing the working electrode to the visible maximum in the solar spectrum. We have conducted coulostatic-flash studies of dye-sensitized photo-oxidation at n- TiO_2 electrodes. Also, because direct excitation of the semiconductor can occur with sub-bandgap irradiation, albeit at lower efficiency, it was necessary to study those processes to distinguish them from dye-sensitized processes. For these studies it was very useful to utilize our high power Xenon flash-pumped dye laser (~1 joule, 500 nS pulses), as the processes were relatively inefficient.

Sub-band gap residual photocurrents at n-type TiO_2 single crystal semiconductor electrodes were studied by comparing the steady state photocurrent and time-resolved (200 nsec) pulsed photovoltage signal under various potential, solution, wavelength and electrode dopant level conditions. The principal electrochemical technique employed in the pulsed experiments was coulostatic chronopotentiometry. Two different photocurrent pathways were discovered involving (a) the presence of surface states from crystal imperfections and (b) the presence of chemically modified (solution dependent) surface states. Only the former process resulted in faradaic electron transfer while the latter produced large coulostatic photovoltages over a narrow electrode potential region (~200 mV). The chemically modified surface states appear to arise from a small cathodic dark process which occurs at ~500 mV positive

of the flat band potential. When the potential is ~200 mV positive of this region the effects are removed (presumably by re-oxidation of the surface species). Thus, their effect is only observed near E^0 for the surface redox process (E^0_{ss}).

The chemically modified surface states greatly influence the magnitude of $\Delta V_{t=0}$ for a coulstatic-flash experiment conducted near E^0_{ss} , but provide no net contribution to the faradaic photocurrent. Estimation of the initial charge injected into the conduction band following the pulse of light shows that the presence of populated chemical surface states at pH = 13 results in a significantly greater signal than that observed at more positive potentials where these states are presumably empty. After 150 μ sec, however, the net photocharge decays to zero near E^0_{ss} while at more positive potentials it remains nearly constant. Keeping in mind that all of these experiments were conducted with a pulsed dye laser and sub-bandgap light, and assuming that the initial flash injection of electrons into the semiconductor space charge region near E^0_{ss} generates holes in the chemical surface states, the question arises as to whether these holes are energetically reactive enough to cause faradaic oxidation. Attempts to influence the rate of the negative photovoltage decay by adding strong oxidizing agents failed to produce any change in the chronopotentiograms obtained near E^0_{ss} . In particular, the addition of the current doubling agent persulfate, did not alter the decay rate perceptibly except to increase the background cathodic current. A further attempt to influence the chronopotentiograms was made by adding current doubling reducing agents (Tiron and Hydroquinone) to the electrolyte. The results of this addition showed an enhanced photovoltage signal, $\Delta V_{t=0}$, at more positive potentials, but not near E^0_{ss} . This suggests that the

negative step observed at more positive potentials results in faradaic electron transfer while that near E^{0ss} is only due to electron - hole generation in the semiconductor conduction band and surface donor states. In this respect it is interesting to note that the oxidation of the solvent and/or current doubling agent at more positive potentials appears to be instantaneous with the flash, which is consistent with the behavior observed by us with TiO_2 under band gap excitation with 10 nsec resolution.

The failure to perceptibly alter the photovoltage transient near E^{0ss} upon addition of strong oxidizing/reducing agents indicates that no faradaic charge transfer results from the photogeneration of holes in the chemical surface states. Thus, it may be concluded that the large photovoltage transient near E^{0ss} resulting from chemically modified surface states is purely the result of internal electrode charge coupling between high energy surface donor states and the semiconductor conduction band.

Evidence that the relative location of the chemically modified surface states lies in the upper region of the band gap is provided by several observations. In the first place, the fact that potentials no greater than 500 mV positive of the estimated flat band were all that was required to depopulate them, indicates that the surface state Fermi level under a slightly positive electrode bias lies below the surface state energy. Second, the comparable quantum yields for electron/hole pair generation near E^{0ss} with both 440 and 584 nm light points to the fact that the energy difference between the lowest conduction band energy level and the mean surface state energy level is not large enough to prevent the longer wavelength light from supplying the necessary energy to make these transitions. (Indeed, the small signal observed with 685 nm light at pH = 13 may indicate the upper bounds of these surface states.) Finally, the inability of holes generated

within these states to oxidize either water ($E_0 \approx .99$ vs SCE) or the reducing agents hydroquinone and Tiron ($E_0 \approx .46$ and 0.6 V vs SCE respectively) places the states energetically within the upper half of the band gap.

One aspect still unanswered at this point is the origin of the surface donor states responsible for the solution photooxidation. One likely explanation is that these states correspond to a disturbed crystal region at the electrode surface which is brought about by the mechanical polishing process used during electrode fabrication. Although the etching procedure should remove a large portion of this disturbed crystal layer, it is doubtful that complete removal is possible so that the single crystal semiconductor remains perfectly ordered up to the interface.

In order to verify this explanation single crystal electrodes were fabricated from the same reduced TiO_2 wafers, but without undergoing the etching procedure. Comparison of flash chronopotentiograms with their etched electrode counterparts shows that only the magnitude of $\Delta V_{t=0}$ in the more positive potential region is increased upon introduction of "mechanical" surface states, and that all other observations are identical with their etched counterparts.

One interesting trend in the pulsed photovoltage behavior of unetched electrodes was the increase in net flash photocharge at positive potentials with decreasing doping level. Similar results with $\text{Ru(III)(bipy)}_3^{3+}$ sensitized photocurrents at variously doped SnO_2 electrodes have recently been reported by Memming, et al. They attributed this behavior to the increased probability of conduction band-surface state electron tunneling as the width of the space charge region decreases with higher dopant density.

Assuming that this process indeed occurs, it is interesting that addition of the doubling agent Tiron to the electrolyte more than tripled the $\Delta V_{t=0}$

response with a highly-doped unetched TiO_2 electrode over that observed without Tiron. Given the irreversibility of the first Tiron oxidation step, it is evident that holes formed in surface mechanical states may rapidly cause a faradaic reaction at a rate faster than the reverse tunneling step. The fact that the photovoltage signal exhibits no additional time dependent change other than the $\Delta V_{t=0}$ step coincident with the flash shows that the faradaic oxidation of both the solvent and Tiron, as well as the reverse tunneling reaction, occurs in less than 200 nsec.

Finally, in order to study dye-sensitized photooxidation processes at n-type TiO_2 semiconductor electrodes, the chromophore Rhodamine B (RhB) was added at various concentrations to the 0.01 M Tiron solutions at pH = 1.2. Except for an enhanced $\Delta V_{t=0}$ step, the time dependence and potential decay of the chronopotentiograms following the 584 nm flash were identical to those observed without RhB. No signal change with RhB was observed in the potential region around or negative of E^0_{ss} . These results show that signals larger by factors of 3 to 10 over those observed without the added dye were obtained at positive potentials with concentrations as low as 2×10^{-5} M. The concentration dependence of the signal change followed a Langmuir adsorption profile (Figure 4) according to the relationship given below.

$$\Delta V_{t=0} \propto \frac{K_{ads} C_{dye}}{1 + K_{ads} C_{dye}}$$

This indicates that only the dye on the surface of the electrode was oxidized with each flash.

There are several significant observations here. First, the adsorbed dye enhances the photocurrent greatly over that obtained directly from surface state excitation. Second, the rise time of the transient photopotential is no

Figure 4

$\Delta V_{t=0}$ vs RhB Concentration for Electrode U_{II} at Various V_{APPL}

584 nm Light

0.1 M H_2SO_4 , 0.01 M Tiron

A - +0.8 V vs SCE

B - +0.6 V vs SCE

C - +0.4 V vs SCE

D - +0.2 V vs SCE

larger in the presence of the dye, indicating that the super-sensitizer, Tiron, reacts rapidly on the 500 ns time scale of the laser pulse. And, third, in the region where chemically-modified surface states exist, the excited dye may be effectively quenched, or else the photooxidized dye may be quickly reduced by electron tunnelling through these surface states. More work needs to be done in this area, including the use of shorter laser pulses, the examination of a variety of dyes, and the use of electrodes with different surface state energy levels.

COMPLIANCE WITH CONTRACT REQUIREMENTS

This Investigator has complied with all of the stated contract requirements.

APPROXIMATE PERCENTAGE OF TIME DEVOTED BY PRINCIPAL INVESTIGATOR

20% of academic year (9 1/2 months)

30% of summer session (2 1/2 months)

REPORTS, PREPRINTS, AND PUBLICATIONS

1. "Laser-Induced Photoelectrochemistry: Scavenging of Photoemitted Electrons in Aqueous and Non-Aqueous Solutions by Electroactive Organic Species", J. H. Richardson, L. J. Kovalenko, S. B. Deutscher, J. E. Harrar, and S. P. Perone, J. Electroanal. Chem., 106, 263 (1980).
2. "Laser-Induced Photoelectrochemistry: Coulostatic Measurements of Photoemission in Aqueous and Non-Aqueous Solutions", J. H. Richardson, S. B. Deutscher, A. S. Maddux, J. E. Harrar, D. C. Johnson, W. L. Schmelzinger, and S. P. Perone, J. Electroanal. Chem., 109, 95 (1980).
3. "Laser-Induced Photoelectrochemistry: Time-Resolved Coulostatic-Flash Studies of Photo-oxidation at n-TiO₂ Electrodes", S. P. Perone, J. H. Richardson, S. B. Deutscher, J. Rosenthal and J. N. Ziemer, J. Electrochem. Soc., 127, 2580 (1980).

4. "Laser-Induced Photoelectrochemistry: Time-Resolved Coulostatic-Flash Studies of CdS Electrodes", J. H. Richardson, S. P. Perone, S. B. Deutscher, J. Phys. Chem., in press.
5. "Laser-Induced Photoelectrochemistry: Time-Resolved Luminescence Studies of CdS Electrodes", J. H. Richardson, S. P. Perone, L. L. Steinmetz and S. B. Deutscher, Chemical Physics Letters, in press.
6. "Pulsed Laser-Induced Photoelectrochemistry at Polycrystalline and Single Crystal Semiconductor Electrodes", S. P. Perone, J. Rosenthal, J. Ziemer, S. B. Deutscher and J. H. Richardson, Proceedings of the Discussions of the Faraday Society. Photoelectrochemistry. Faraday Discussion #70, in press.
7. "Cyclic Voltammetry and Pulsed Photocurrent Measurements at Irradiated Single Crystal and Polycrystalline Semiconductor Electrodes", J. Rosenthal, A. D. Kupfer, J. M. Martin, S. P. Perone, J. Electroanal. Chem., Submitted.
8. "Laser-Induced Sub-bandgap Photocurrents at Single Crystal n-TiO₂ Semiconductor Electrodes", J. N. Ziemer and S. P. Perone, J. Phys. Chem., Submitted.