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The last year's work has focussed on several aspects of the fundamental chemistry and physics semiconductor/liquid junction behavior. These projects have been directed primarily towards GaAs/liquid contacts, because GaAs/liquid systems provide high energy conversion efficiencies and offer an opportunity to gain mechanistic understanding of the factors that are important to control in an efficient photoelectrochemical energy conversion system. A summary of our recent results in each individual area is described below.

I. Time-Resolved Photocurrent Measurements at Semiconductor/Liquid Interfaces

We have undertaken an extensive study of time-resolved photocurrent measurements at semiconductor/liquid interfaces. Although in the last decade there have been numerous measurements of time-resolved photocurrents at semiconductor/liquid interfaces, there is still controversy regarding the fundamental interpretation of the time-resolved current that is induced by a brief laser pulse onto a semiconductor/liquid contact. For instance, there are currently at least six different equivalent circuit representations proposed for this system, with each equivalent circuit resulting in a different fundamental interpretation of the measured current in terms of the interfacial resistances and capacitances of concern in the actual solid/liquid interfacial system. Bocarsly and co-workers have interpreted transient photocurrent decays at TiO_2 anodes in terms of rate-limiting hole transfer processes and have reported kinetic isotope effects to support this interpretation, while other workers have claimed that interfacial charge transfer cannot be determined using this method and that system capacitances and series resistances will be determined from the transient current response. Still other workers have offered additional, alternative interpretations of this data, and the interpretation is therefore quite unresolved to date. We have exploited some of the unique aspects of semiconductor/liquid junctions in nonaqueous solvents to distinguish experimentally between these different possibilities, and have performed experiments that will clarify the theoretical and experimental interpretation of time-resolved photocurrent measurements at solid/liquid interfaces.

To probe these different predictions, we have taken advantage of our experience with preparing stable, efficient photoelectrochemical cells based on GaAs, Si, and similar materials in non-aqueous solvents. Furthermore, for Si, previous measurements have shown that the carrier concentration decays in contact with the dimethylferrocene $(Me_2Fc)^{+/0}$ redox system are rather slow, >200 μsec, and this unusually long charge transfer time would provide an ideal system to distinguish between several of the different types of equivalent circuits for interpretation of time-resolved photocurrent measurements with no complications from system-response limited decays due to the measuring electronics or cell time constants themselves.

The system was probed using a mode-locked dye laser that was synchronously pumped with a cw Nd:Yag laser. The dye laser provided tunable red pulses of 9 ps in duration; the light intensity was reduced with neutral density filters until the decay times of the transient photocurrent signals were independent of further changes in light intensity. Potential excursions at these light intensities were typically less than 20 mV. Photocurrents were amplified and then measured using a transient digitizer, followed by signal averaging and then analysis using standard routines. Signals were excellent single exponential decays, even on timescales <1 μs in our electrochemical cell setup.

In this system, if the photocurrent decay truly reflected the interfacial charge transfer kinetics, then we would expect, based on prior measurements, that a decay of 100-

200 μsec would be observed in the transient photocurrent measurement. However, we observed much shorted time constants for the decays, with typical values of <1 μsec through a 50 ohm external measuring impedance. Furthermore, these values increased linearly with changes in the value of the external load resistance, and were entirely consistent with limitations on the transient photocurrent being due to fundamentals of the cell response as opposed to interfacial charge transfer events. An equivalent circuit representation, similar to that proposed by Willig and co-workers, has been developed that is consistent with all of our results, and a physical justification for this circuit has been obtained that is consistent with interfacial behavior observed in other experiments on such systems.

To further verify that the signals were not influenced by the interfacial charge transfer rates across the Helmholtz layer, several other experiments were performed using different concentrations of redox couples, different semiconductors, and comparing semiconductor/metal junctions to semiconductor/liquid interfaces under otherwise similar circumstances. These experimental results are all consistent with our equivalent circuit approach, and appear to satisfactorily reconcile the discrepancies in the various interpretations of time-resolved photocurrent measurements that are now in the literature. This work is being finalized for publication at present, and the full manuscript contains the entire details of our work in this area.

II. Studies of the Passivation of GaAs Surface Recombination

We have also completed a very lengthy, complete study of the surface passivation effects of GaAs surfaces due to exposure to thiols and aqueous inorganic sulfide solutions. We have determined that a series of organic thiols and amines can yield a substantial reduction in nonradiative surface recombination at GaAs interfaces, as measured by steady state photoluminescence experiments, and have explored in depth the surface chemistry and physics of these chemisorption steps.

Treatment of the air-etched GaAs surface with $Na_2S{\bullet}9H_2O$ has been reported previously to reduce the low level injection value of the surface recombination velocity, S , for GaAs from $>10^5$ cm/sec to 10^3 cm/sec, and our steady-state photoluminescence (PL) data was in accord with this observation. We also observed that exposure to alkyl and aryl thiols (1-chlorothiophenol, 1,2-dithiolethane, 1-butanethiol), deprotonated alcohols (sodium methoxide and sodium phenoxide) and amines (ethylenediamine, 1,8-bis(dimethylamino)naphthalene) effected large reductions in the low level injection S value; furthermore, the effects of the thiols were comparable in magnitude to the $Na_2S{\bullet}9H_2O$ (aqueous) treatment . In addition to demonstrating that a class of thiols is effective in reducing the recombination velocity of GaAs surfaces, the data yields valuable chemical information concerning the nature of the important nonradiative surface recombination centers. While simple unhindered aryl and alkyl thiols were effective in reducing the surface recombination velocity, additional experiments with weak donors, such as thiophene (C_4H_4S) and dimethylsulfide ($(CH_3)_2S$), indicated that such compounds did not effect a large change in the PL signal. This trend parallels that commonly observed for the binding constants of sulfur ligands with transition metal Lewis acid centers,and is consistent with the hypothesis that effective coordination to the recombination site is an important component of improving the PL signal. Additionally, the preliminary trend in PL intensity observed for the various heteroatom bases of S>N,O suggests that the surface site is "soft" in character and prefers polarizable ligands, as opposed to being protic in character and being only sensitive to the pK_a of a compound. This would be expected for a polarizable, electron deficient site, such as perhaps As^0, or possibly Ga atoms in a GaAs lattice, but is not consistent with expectations for an oxide-type acceptor site.

To determine the composition of the $Na_2S{\bullet}9H_2O$ (aq) and thiol-treated GaAs surfaces after the different etches, a series of high resolution X-ray photoemission spectra on thoroughly rinsed GaAs surfaces were collected. XPS experiments were performed on 10^{17} doped bulk (100) n-GaAs. The contributions of various surface species to the As 3d and Ga 3d regions were determined using standard curve-fitting techniques. As expected, the GaAs surface exposed to etch B displayed a large (~3×10^{-9} mole/cm^2) coverage of excess As^0; the As^0 was introduced deliberately in the etching process so that its subsequent reactivity with the sulfide and thiol solutions could be easily monitored by XPS.

Monochromatic Al Kα XPS data for the As 3d regions of GaAs surfaces of varying initial compositions revealed essentially the same surface after exposure to 1.0 M $Na_2S\bullet9H_2O_{(aq)}$. Consistent with prior work, near-monolayer coverages of As_2S_3-type phases were readily observed after exposure of GaAs to 1.0 M $Na_2S\bullet9H_2O_{(aq)}$.. On a surface that had been treated to yield a large amount of elemental As, essentially all the As^0 was effectively removed by the aqueous sodium sulfide solution. Exposure to 1.0 M 4-chlorothiophenol in diethyl ether resulted in the presence of persistent Cl signals, indicating that the 4-chlorothiophenol had adsorbed on the GaAs surface, However, XPS measurements indicated that adsorption of the 4-Cl-thiophenol but did not result in elimination of excess As^0. Additionally, no detectable As_2S_3 (<1×10^{-10} mol As_2S_3-cm^{-2} surface coverage) or other As-S type oxidized As signal was observed on the thiol-exposed GaAs surface. The lack of As_2S_3 formation and residual presence of As^0 was also verified for exposure to other thiols, including 1,2-dithiolethane and 1-butanethiol. In fact, the only systematic change in the XPS detectable on thiol-treated GaAs surfaces was due to XP lines from the thiol itself; this result was verified even on stoichiometrically etched (etch A) surfaces that had little or no detectable As^0, As-oxides or Ga-oxides before immersion into the thiol solutions.

This behavior is not expected based on several hypotheses for the surface chemistry responsible for the $Na_2S\bullet9H_2O$/GaAs passivation process. The removal of excess As^0 and/or formation of an epitaxial, defect free, layer of As_2S_3 have been proposed to explain the improved electrical properties of GaAs that has been exposed to 1.0 M $Na_2S\bullet9H_2O$ (aq). In contrast, the comparable steady state PL intensities for the simple alkyl and aryl thiols, combined with the XPS data for these systems, indicates that effective passivation of GaAs surface recombination can occur without such gross changes in surface stoichiometry. The trends indicate, however, that effective binding to the important chemical recombination site is required, and that S-donors are substantially more effective than "harder", less polarizable, O and N bases.

III. Steady-State Mechanistic Studies of n-GaAs Photoelectrodes in Non-aqueous Electrolytes

We have continued our studies of the current-voltage response of GaAs anodes that have been exposed to solution of group VIIIB transition metal ions and then immersed into aqueous 1.0 M KOH-0.8 M Se^{2-}-0.1 M Se_2^{2-} solutions. There is now little doubt that the dominant mechanism of I-V in this electrolyte is electrocatalytic acceleration of the minority carrier charge transfer rate into the $Se^{-/2-}$(aq) redox system. This hypothesis would predict that the I-V properties of GaAs electrodes in contact with outer sphere redox reagents in nonaqueous solvents would not be affected by the chemisorption of transition metal ions. We have investigated this aspect of GaAs photoelectrochemistry in the past year.

GaAs photoanodes were exposed to aqueous solutions containing $Co(III)(NH_3)_6^{3+}$, Ru(III), Rh(III), and Os(III) ions, and were then evaluated either in contact with 1.0 M KOH-0.8 M Se^{2-}-0.1 M Se_2^{2-}(aq) solutions or with CH_3CN solutions that contained metallocene (M=Co, Fe) reagents or viologens. The CH_3CN solutions each exhibited a characteristic set of I-V properties that were unique to the redox reagent/solvent combination, and for the case of ferrocene/CH_3CN, prior exposure to metal ion solutions or to metal ions and then KOH-$Se^{-/2-}$(aq) solutions did not affect the I-V properties. This is consistent with the hypothesis that the metal ions have an electrocatalytic effect, because a Schottky barrier junction would have yielded the same I-V curves regardless of whether the contact was the aqueous selenide system or the nonaqueous metallocene system, and this invariable of I-V properties with the nature of the contact was not observed for metal-ion-coated GaAs photoelectrodes.

In contact with other redox reagents, however, the I-V behavior was more complicated. In particular, exposure to solutions of cobaltocene produced changes in I-V properties in the aqueous KOH-$Se^{-/2-}$ electrolytes, presumably due to chemisorption of small amounts of Co impurities in the cobaltocene solutions. However, although these electrodes yielded the expected behavior in contact with the aqueous solutions, the I-V properties of these surfaces that had been subsequently evaluated in contact with CH_3CN/ferrocene electrolytes were different than those observed from simple immersion into $Co(III)(NH_3)_6^{3+}$ solutions. At present, therefore, the surface chemistry is more complicated than originally anticipated, and only the ferrocene/CH_3CN system presents an unambiguous system for evaluation of the electrocatalytic hypothesis. Without direct spectroscopic information on the chemical nature of the interface both before and after metal ion chemisorption, it will be difficult to ascertain the origin of these metal-ion-induced changes in I-V properties in the cobaltocene-containing solutions; this spectroscopic information will be obtained in the next project period on our newly installed ultra-high vacuum surface spectroscopic chamber that was obtained for this purpose with funding from the DOE University Instrumentation Program. Further information regarding the surface chemistry of GaAs and other photoelectrode systems will be performed using this instrumentation, and these experiments will be some of the main focus for work to be performed in the next project period.

Papers Under DOE Support, 1991-92 Project Period

Bruce J. Tufts, Louis G. Casagrande, Frank J. Grunthaner, and Nathan S. Lewis, "Correlations Between the Interfacial Chemistry and Current-Voltage Behavior of n-GaAs/Liquid Junctions ", *Appl. Phys. Lett.*, **57**, 1242 (1990). Counted last year

Louis G. Casagrande, Bruce J. Tufts and Nathan S. Lewis, "Trends in the Open Circuit Voltage of Semiconductor/Liquid Interfaces: Studies of n-$Al_xGa_{1-x}As/CH_3CN$-Ferrocene$^{+/0}$ and n-$Al_xGa_{1-x}As$/KOH-Se^{2-} (aq) Junctions," *J. Phys. Chem.*, **95**, 1373, 1991. Counted last year

✓ Sharon R. Lunt, Patrick G. Santangelo and Nathan S. Lewis, "Passivation of GaAs Surface Recombination with Organic Thiols", *J. Vac. Sci. Tech.*, **9**, 2333 (1991).

✓ Nathan S. Lewis, "An Analysis of Charge Transfer Rate Constants for Semiconductor/Liquid Interfaces", *Ann. Rev. Phys. Chem.*, **42**, 543 (1991).

✓ Ming Tan, Charlotte Newcomb, Amit Kumar, Sharon R. Lunt, Michael J. Sailor, Bruce Tufts, and Nathan S. Lewis, "Chemical Modification of n-GaAs Photoanodes with Group VIIIB Metal Ions: Stability in Contact with 1.0 **M** KOH(aq)-0.10 **M** K_2Se(aq) Solutions and I-V Properties in Contact with 1.0 **M** KOH(aq)-1.0 **M** K_2Te(aq) Electrolytes", *J. Phys. Chem.*, **95**, 133 (1991).

✓ Sharon L. Lunt, Gail N. Ryba, Patrick G. Santangelo and Nathan S. Lewis, "Chemical Studies of the Passivation of GaAs Surface Recombination Using Sulfides and Thiols", *J. Appl. Phys.*, i~~n press.~~ 70, 7449 (1991).

Biographical Information--Nathan Saul Lewis
Professor of Chemistry, California Institute of Technology

A. Identifying Data:

1. Born: October 20, 1955, Los Angeles, California
2. Nationality: USA

B. Complete Academic History

1. California Institute of Technology, 1973-77
   B.S. in Chemistry with Highest Honors, 1977
   GPA 4.0/4.0

   M.S. in Chemistry, 1977
   Thesis Title: "The Chemistry of Rhodium and Molybdenum Isocyanide Complexes"
   Advisor: Professor Harry B. Gray

2. Massachusetts Institute of Technology, 1977-81
   Ph.D. in Inorganic Chemistry, 1981
   Advisor: Professor Mark S. Wrighton
   Thesis Title: "Manipulation and Measurement of Charge Transfer Kinetics at Chemically Modified Electrodes"

3. Scholarships and Academic Honors
   California State Scholarship Recipient, Caltech, 1976-77.
   Achievement Rewards for College Scientists Foundation Scholarship, Caltech, 1975-77.
   Carnation Company Academic Merit Scholarship, Caltech, 1976-77.
   Sigma Xi Undergraduate Research Award, Caltech, 1977.
   Fannie and John Hertz Foundation Fellow, MIT, 1977-81.

C. Employment Record

1. Full-time positions
   Research Assistant, California Institute of Technology, 1974-77.
   Research Assistant, Massachusetts Institute of Technology, 1977-81.
   Assistant Professor, Stanford University, 1981-1986.
   Associate Professor, Stanford University, 1986-1988.
   Associate Professor, California Institute of Technology, 1988-1991.
   Professor of Chemistry, California Institute of Technology, 1991-present

2. Consultantships
   Lawrence Livermore National Laboratory Livermore, CA 1977-81, 1984-present.
   Solar Energy Research Associates, Santa Clara, CA 1981-85.
   American Hospital Supply, Irvine, CA 1983-85.
   Molecular Devices, Palo Alto, CA 1983-present.
   Member, JASON, The Mitre Corporation, McLean, Virginia, 1990-present.

D. Public and Professional Service

Divisional Editor, Journal of the Electrochemical Society, 1984-1990.
U.S. Japan Joint Conference on Photochemistry and Photoconversion, 1983.

NATO Workshop on Photocatalysis, 1985.
IDA Defense Science Study Group, 1985, 1986.

E. Post-degree Honors and Awards

Camille and Henry Dreyfus Teacher-Scholar, 1985-1990.
Alfred P. Sloan Research Fellow, 1985-1987.
IBM Young Faculty Development Award, 1983-85.
Presidential Young Investigator Award, 1984-present.
1990 Fresenius Award of Phi Lambda Upsilon
1991 ACS Award in Pure Chemistry

F. Research Interests

Charge separation processes at the semiconductor/liquid interface. Photoelectrochemical processes for the conversionand storage of solar energy. Fundamental interfacial chemical reactions of semiconductor/liquid and semiconductor/metal and semiconductor/conducting polymer contacts. Development of the coordination chemistry of semiconductor surfaces. Novel electrochemical reactions at chemically modified surfaces.

Funding Amounts and Relationship to Other Existing and Proposed Funding

Existing Grants

NSF: $41,000 direct costs, 1991-92; 10% PI time. *Chemical Control of Recombination at Semiconductor Interfaces.* Supports 1.0 graduate students at present funding level and salary expense rate. A renewal proposal for this grant is in preparation. The work involves mechanistic studies of Si/liquid interfaces for photoelectrochemistry. The NSF work does not include fast transient studies on Si reported herein.

DARPA: 5% PI time. *"Fundamental Studies on C-H Activation For Alkane Fuel Cell Applications"* Lewis is one of 6 co-investigators on project to develop electrocatalysts for methane oxidation to CO_2; PI is H.B. Gray. Grant supports 1.0 post-doc in my group at present; no relationship to this proposed work at all.

ONR: $27,800 direct costs, 1991-92; 5% PI time. *Applications of Scanning Tunneling Microscopy to Electrochemistry:* To probe electrode surfaces using STM/AFM methods, and to study microelectrode behavior. Grant in final year, to be terminated in 1992 according to program director, due to DoD budget cuts. Current "wind-down" funding level supports ≈0.7 graduate student. This proposal is for continuation of this work under the NSF/EPRI Initiative in Electrochemistry.

DOE: $69,600 direct costs, 1991-92; 10% PI time. *Picosecond Dynamic Studies of Electron Transfer Rates at III-V Semiconductor/Liquid Interfaces.* Supports 1.0 graduate student, and ≈1 post-doc. This DOE grant supports time-resolved kinetic studies of GaAs and other III-V semiconductor/liquid interfaces.

Petroleum Research Foundation: $18,000 direct costs, 1991-92; 5% PI time. *Cyclic Voltammetry of Semiconductor Electrodes.* Supports 0.5 graduate student to develop theory and experiment of cyclic voltammetry at semiconductor electrodes. No direct relationship to this proposal.

National Science Foundation: $40,000 direct costs, 1991-92; 5% PI time. *Development of Computer Graphic Visualization Aids for the Undergraduate Chemistry Curriculum.* Lewis is PI;

8 co-investigators in this Caltech curriculum development/educational effort. Supports 6 undergraduates for development of computer-based graphics animation for undergraduate education in chemistry. No research component of this grant; no overlap with proposed research work at all; no faculty salary, travel, or secretarial support in this grant.

Proposed Funding

GRI: $76,000 direct costs 1991-92; 10% time. *H_2S Processes Involved in Liquid Redox Chemistry:* To investigate mechanisms of H_2S oxidation based on transition metal complexes. No relationship to this proposed work at all.

NSF Materials Chemistry Initiative: $203,890 direct costs, 1991-92; 7% time *Novel Materials From Conjugated Polymers:* proposal submitted and under review; co-PI Robert Grubbs; Lewis is P.I. for Materials Resource Center in Caltech's Beckman Institute, in which work will be conducted. Work involves use of conducting polymers to make novel electronic and optical device structures. No direct relationship to this project. Proposed support for 2 graduate students and 2 post-docs between the two PI's.

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