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MONITORING INTERFACIAL DYNAMICS BY PULSED LASER TECHNIQUES

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Appendix 2: PROGRESS REPORT COVERING PREVIOUS BUDGET PERIOD
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Monitoring Interfacial Dynamics by Pulsed Laser Techniques

1. Technical Summary of Research Activity

The reactivity of semiconductor surfaces can influence the performance of the semiconductor, usually in an adverse manner. In a reactive environment, such as immersed in an electrolytic solution, surfaces such as Si, Ge, and GaAs can readily react with their environment to produce unwanted surface species including surface oxides and surface defects. Often such reactive processes diminish the efficiency of the semiconductor in performing a particular task. The research in our laboratory currently supported by DOE is aimed at understanding the structural, electronic and reactive properties semiconductors in solution environments. In particular, our focus has been on Si and GaAs surfaces because of their current and potential use in photovoltaic devices and other electronic applications. We have made considerable headway in providing unique new information about the behavior of these surfaces in electrochemical environments and in UHV. Our approach has been to employ pulsed laser techniques, particularly surface second harmonic generation (Si studies) and laser induced photoluminescence (GaAs studies). In the Si studies, we have demonstrated the unique sensitivity of the phase of the SH response to space charge effects.^{1,2} With GaAs, we have used time-correlated single photon counting methods in the picosecond time regime to examine the recombination luminescence following above band gap excitation.³⁻⁹ The sections below outline our most significant accomplishments in our work.

(a) SHG Studies of Si/Electrolyte and Si/SiO₂/Electrolyte Interfaces

An increased understanding of surface reactivity and stability in electrolytic solutions in recent years has been gained through infrared reflectance,^{10,11} ultra-high vacuum (UHV) transfer experiments, scanning tunneling microscope (STM)¹²⁻¹⁶ and atomic force microscope (AFM)¹⁷ imaging, and SHG.^{2,18-21} This progress can be attributed both to improved experimental methodologies as well as to advances in surface preparation procedures, e.g. hydrogen termination of the silicon surface.¹¹ However, these studies have only begun to describe the complex behavior of Si electrodes and the properties of the depletion layer. The use of SHG as a probe of interfacial electronic properties of semiconductors extends back to some of the earliest work of SHG on interfaces.^{18,22} Recently, our group^{1,2,23} as well as several others¹⁹⁻²¹ have returned to examining in more detail the SH response from silicon immersed in electrolyte systems in an attempt to exploit the inherent sensitivity and temporal response of the technique as an in-situ probe.

Characterization of the silicon surface in a reactive environment and the Si/SiO₂ interfacial region has proven to be extremely complex and is therefore widely represented in the literature. The width, composition, and structure of this transition layer continue to be topics of discussion in the literature. Recent advances in the chemical wet etching of the Si(111) surface predominantly characterized by multiple internal reflection infrared spectroscopy has led to an improved understanding of the "clean" silicon surface as well

as providing a relatively simple preparation procedure for obtaining such a surface.¹⁴ The "clean" surface, which is obtained at room temperature by etching the native surface oxide in an $\text{NH}_4\text{F}/\text{HF}$ solution buffered to pH 8 (by addition of NH_4OH) followed by a thorough water rinsing, has been shown to be atomically smooth with large ideally mono-H-terminated terraces and two atom step edges. Furthermore, these surfaces are relatively stable in air and immersed in solution (until driven to oxidation under anodic bias). In contrast, surfaces etched only in HF result in mono-, di-, and tri-H-termination and exhibit microscopically rough surfaces. Higashi *et al.*¹⁴ observed that these surfaces exhibit reversible surface roughening or smoothening if immersed in HF then in the buffered $\text{NH}_4\text{F}/\text{HF}$ solution, respectively, or vice-versa. Thus, the roughening observed with an HF etch does not reflect the morphology of the initial Si/SiO₂ interfacial region, but is instead a result of the etching process.

Our studies have been conducted with two primary objectives in mind. The first has been to determine if the intensity and phase of the SH optical response is sensitive to potential induced variations in the static field applied to the semiconductor/electrolyte interface, and related to this, how the presence of oxide layers of varied thicknesses on the Si(111) surface alters this potential dependence. Because semiconductors can have a relatively large bulk response, it has not been clear whether any significant potential dependence can be observed from the semiconductor surface region. Unlike metal electrodes where SHG is highly sensitive to potential variation due to the screening of the charge at the surface,^{24,25} the field for semiconductors can extend several hundred angstroms into the material, the depth dependent upon the doping density of the semiconductor, possible Fermi level pinning and the strength of the applied field. Also of question is whether one can observe significant differences in the potential dependence between an oxide-free surface (in this case a H-terminated surface), and a surface with trace oxides present.

The second focus of our study has been of a more fundamental nature. That is, to address issues related to the source of the response from these buried interfaces including determining the coupling of the applied static field to various susceptibility tensors, and understanding the relative contribution from parts of the interfacial region such as the depletion layer, the Si(111) surface adjacent to the electrolyte or oxide, and the SiO₂ layer. Potential dependent measurements are an important means of examining such questions since the interfacial region can so readily be altered by potential variation.

In our first letter published on this work,² our SHG results of Si(111) surfaces in electrolytic solutions showed a highly potential dependent response for H-terminated n-Si(111) surfaces biased in NH_4F and oxide covered surfaces biased in H_2SO_4 . This and much of our later work has involved measuring the variation in the SH response with azimuthal rotation of the sample by 360° about its perpendicular axis. Such rotational anisotropy measurements which are conducted with selected input and output polarizations can provide valuable insight into the amplitude and phase of the SH response as interfacial properties are altered.

Figure 1(a) shows the p-polarized SH response from H-terminated n-Si(111)

Fig. 1. SH rotational anisotropy from n-Si(111) immersed in 0.1 M NH_4F at flatband and depletion conditions. All scans were taken with p-input and p-output polarizations. The solid lines is the fit to the data with the derived values for $c^{(3)}/a$ given in the figure.

biased at the flatband. A 10 nsec pulse of p-polarized 1064 nm light was used with the SH response collected at 532 nm. The anisotropy patterns are fit using a phenomenological description.²⁶⁻²⁸ The fit provides a ratio of two phenomenological constants, $c^{(3)}/a^{(\infty)}$ which contains both a relative magnitude (2.2) and a relative phase (21°) which is indicative of the extent of interference between the anisotropic and isotropic components.

The SH rotational anisotropies from this surface show that the overall SH response is highly potential dependent. As shown in Figure 1 (a-d), a small increasing trend is observed in both the relative amplitude with a dramatic change in the phase angle as the sample is biased from flatband into depletion conditions. We attribute this to the change in the static field at the surface and within the space charge region (SCR) of the silicon sample, a $\chi^{(3)}$ type effect where the applied static field couples to the optical fields.²⁹⁻³¹ The nonlinear response contains contributions from both the surface dipolar and higher order bulk quadrupolar sources, which have been determined to be approximately equal in magnitude. Thus, the SH response can indeed be sensitive to a

change in the "bulk" properties of the semiconductor, such as the creation of a depletion layer and an increase in the depletion layer width as the potential is driven anodically. The depletion layer can be viewed as a region of electronic asymmetry; thus, this asymmetric region of the sample strongly contributes to the response. These studies furthermore suggested that the phase of the anisotropy in the SH response could be correlated with the dc field strength in the space charge region. The field strength in the space charge region is otherwise a difficult property to measure for these semiconductor/electrolyte systems. One reproducibly observes a phase angle of 21° when the H-terminated surfaces is biased at the flatband. As shown, as the field strength is increased progressively to a bias of 1.65 V positive of FB, the phase angle also progressively rises to 126° .

Over the past year we have expanded the study to Si(111)/SiO₂/electrolyte, Si(111)/vacuum, and Si(111)/SiO₂/vacuum interfaces.²³ For the oxidized surface it is found that the relative phase between the in-plane and out-of-plane response behaves consistently with the H-terminated studies. To make a direct comparison however, we have had to develop a means of accurately determining the flatband potential for the

Fig. 2. SH rotational anisotropy from n-Si(111)/SiO₂ ($\sim 40\text{\AA}$) immersed in 0.1 M H₂SO₄ at flatband and depletion conditions. All scans were taken with p-input and p-output polarizations. The solid line is the fit to the data with the derived values for $c^{(3)}/a$ given in the figure.

oxidized surfaces. By taking photocurrent transient data concurrently with the SHG measurements we have been able to obtain a reasonably accurate flatband potential. Figure 2 shows our results for samples for which a layer of oxide of approximately 40Å is present. Consistent with the H-terminated studies of Figure 1, as the band are increasingly bent (depletion condition), by the application of the applied dc field, the relative phase progressively increases. The initial phase angle of approximately 40° is characteristic of all oxidized samples of various layer thicknesses as long as the potential is held at the flatband for the particular sample. The most significant difference between the data in Figs. 1 and 2 is that it takes a much larger field strength applied across the oxidized sample to obtain comparable changes in the phase angle, ie. 3.5 V for the oxidized sample compared to 1.65 V for the H-terminated surface. If the phase angle is truly sampling the strength of the field in the semiconductor, or the width of the depletion layer, this would suggest that the field strength within the oxidized sample is smaller than that of the oxide free surface for any given potential. This is exactly what one would expect due to the insulating nature of the oxide overlayer. We have further extended this analysis in solution for oxides grown either thermally or by electrochemical photooxidation of the semiconductor.

In summarizing the work to date, our studies suggest that SHG has the unique ability to measure space charge effects in the semiconductor under a variety of conditions, ie. immersed in an electrolyte, in the presence oxide overlayers, and under UHV conditions. In our future studies we would like to explore this more detail so as to be able to make more quantitative descriptions of depletion layer conditions for Si samples in a variety of conditions and in the presence of various overlayers.

(b) Photoinduced Processes at the n-GaAs/Electrolyte Interface

Understanding the reactivity of semiconductor/liquid junctions upon photoexcitation has been the focus of the second part of our DOE funded research over the past several years. Such studies have significance to photovoltaic technology as well as to improved semiconductor processing in aqueous and nonaqueous environments. We have had particular success in our understanding of reactive processes at GaAs/electrolyte interfaces. Our approach has been to monitor the photoluminescence which results from above band-gap excitation with picosecond pulses.^{5-8,32} The temporal response and the potential dependent response in the photoluminescence is then used to understand the carrier dynamics which control the reactivity of the semiconductor surface.

A focal point of the work has been to study the rate of nonradiative recombination of carriers at the surface, referred to here as surface recombination or surface trapping velocities (STVs). Surface traps can play a central role in determining the efficiency of a photoelectrochemical device. The surface traps which can be present due to surface defects, dangling bonds and adsorbed surface species can act as mediators in the transport of carriers across the interface but can also diminish the efficiency of the device by acting as recombination centers for the photogenerated holes. Measurement of the rate of filling of these traps, when coupled with photocurrent and photocapacitance data, can provide a powerful means of elucidating carrier dynamics over a range of potentials, surface conditions and electrolyte composition. In the recent past, STVs have primarily been

derived from examining the potential dependence of the photoluminescence using above bandgap light from a conventional continuous wave (cw) source. By application of the modified dead layer model (MDLM), Gerischer and others found that one could derive STVs at flatband.³³⁻³⁶ Such measurements have been very useful but can not provide STV's for potentials beyond flatband, ie. depletion and accumulation conditions.

Our goal has been to use short laser pulses (~5 psec pulses) to derive STV's from the PL decays following photoexcitation. The temporal data can provide a more direct measurement of the STVs not only at flatband, but at a variety of potentials. How the measured STV is affected by presence of adsorbed species at the surface, the applied potential and the composition of the electrolyte then provides information about the competing processes which can lead to eventual corrosion of the surface, passivation against surface reactivity, or other interfacial charge transfer processes.

The excitation source used for all experiments is the frequency doubled pulse compressed output of a Nd:YAG laser, with 5 ps pulsewidth and variable repetition rate. All experiments have been performed on n-GaAs (100) having a doping density of $2-4 \times 10^{17}$ (Si). The cell includes a Pt counter electrode and a separate Pt reference electrode which is located near the working electrode. A potentiostat allows control over bandbending as well as a monitor of the photocurrent. A flatband of -1.1 V is expected based on our measurements and a correction of 0.06 V/pH unit.

The results of our PL work has been presented in several recent publications.³⁻⁹ The first studies have been to evaluate the feasibility and accuracy of deriving STVs from pulsed laser excitation in general, and temporal measurements in particular. Such studies of have involved a comparison of the PL response from continuous excitation with pulsed excitation for n-GaAs(100) in a Na₂S containing aqueous electrolyte. The second part of these studies has involved examination of photocorrosion and passivation of n-GaAs in various sulfide containing aqueous electrolyte solutions.

(i) *Comparison of the photoluminescence response as a function of applied potential using a continuous wave and pulsed laser source.* These experiments compared the response from a HeNe laser (cw) and a picosecond Nd:YAG laser (5 psec) of comparable excitation average powers. Figure 3 shows a comparison of the results.

Figure 3. Luminescence intensity versus applied potential. The lower solid curve was obtained using a cw HeNe laser for illumination (0.280 mW average power). The open circles and triangles show the intensity expected in the depletion region using the dead layer model for the 633 and 532 nm experiments respectively.

Both show similar trends in the photoluminescence as a function of potential, lowest PL response under depletion conditions where the minority carriers are driven to the surface, and the highest PL when the holes are driven into the bulk. For both the PL levels off near flatband where one expects field free conditions.

(ii) *Modeling the potential dependence data using the Modified Dead Layer Model.*

We have examined the applicability of the MDLM to the data as a means of obtaining STVs at flatband from photoluminescence vs voltage data. The dead layer model³³⁻³⁶ predicts that, in the depletion regime, the luminescence intensity will depend on the applied potential according to the expression

$$I_{pl} = I^0 \exp(-\alpha W) \quad (1)$$

where I_{pl} is the measured luminescence intensity, I^0 is the luminescence intensity at the flatband potential assuming infinite STV, and α is the absorption coefficient for the semiconductor electrode at the excitation wavelength. W is the width of the depletion layer which is directly related to the difference between the applied potential and the flatband potential. Figure 3 shows the good fit of the data to the MDLM for both HeNe and Nd:YAG laser excitation where the STV is assumed to be infinite. Assumptions in the model only make it applicable to regions where the STV is infinite, ie. the depletion region. Quantitatively, the STVs recovered from luminescence decay profiles are in agreement with the values from the present analysis when a value of the diffusion coefficient which is lower than would be expected from the doping density of our samples used. Here we argue that this effect is also attributable to the picosecond pulse excitation. The dead layer model is based on the assumption that steady state has been achieved. This is, the model assumes that cw illumination is used and that the excitation is present long enough before the measurement begins so that carriers are distributed to a depth on the order of the diffusion length of minority carriers in the material. In experiments using picosecond pulse excitation of relatively short wavelength (compared with the diffusion length), such a steady state is never attained. Carriers are generated over only a small fraction of the diffusion length (about 20% in these experiments), and the initial flux of carriers toward the surface opposes the flow of carriers toward the bulk. Because carriers in the bulk are more likely to undergo radiative relaxation, a lower luminescence intensity can be anticipated under picosecond illumination than for cw excitation.

(iii) *Measurement of STVs from Photoluminescence Decay Measurements.* Once values for the STVs were established from the potential dependent measurements, we conducted time dependent photoluminescence decay measurements to see how the derived STVs compare with the potential dependent measurements of STVs using the MDLM. Deriving STVs from the decay measurements requires fitting the PL decay to a function which contains the STV. We found that a commonly used function for determining such STV values for GaAs in air was inadequate.³⁷ We attributed the inadequacy to the assumption made in the previously used model that the traps, which

can be of varying energies, fill with equal probability. We subsequently built into the model a barrier function which more realistically describes the filling as having a time dependent barrier, ie. the lowest energy trap states fill first. This gave a much improved fit to the data and allowed us to determine values for the STVs at flatband.^{5,6}

Figure 4. Photoluminescence decays of the GaAs electrode held at flat band potential at three excitation power levels: (a) 4×10^{12} , (b) 1×10^{12} and (c) 3×10^{11} (photons/cm²)/pulse. The solid line is a convolution of the system response function with a simulated decay which includes a time-dependent STV.

Figure 4 shows the data obtained for several incident fluences. As shown in the table below, the values obtained at flatband for the three fluences show remarkable agreement with the values obtained in the potential dependent measurements at similar laser average powers. The range shown for the temporal data is due to the uncertainty in the number used in the decay for the bipolar diffusion coefficients.

Table 1: STVs Obtained at Flatband From Decay and Potential Dependent Measurements

Flux (photons/cm ² /pulse)	Decay Measurements STV(cm/s)	Pot. Dep. Measurements STV(cm/s)
4×10^{12}	105,000	105,000 - 170,000
1×10^{12}	170,000	170,000 - 270,000
3×10^{11}	>500,000	infinite

(iv) *Determination of STVs at Various Potentials.* To reiterate, the advantage of the photoluminescence decay measurements are that they provide surface trapping velocities at a series of potentials, not merely at the flatband. Figure 5 shows the photoluminescence decays at -2.0 V (accum), -1.0 V (flatband) and 0 V (depletion). The surface trapping velocities were obtained at a series of potentials with the values derived for the data in Figure 5 determined to be 80,000 cm/s, 105,000 cm/s and 220,000cm/s for

-2.0, -1.0 and 0 V respectively. As expected the STVs increase with increasing bandbending towards depletion conditions.

Figure 5. Photoluminescence decays from the GaAs/Na₂S junctions vs. applied potential. A photon flux of 4×10^{12} photons/cm²/pulse was used. The noiseless lines are simulations using the described model.

(v) *Power Dependent Studies.* In both the potential dependent data and the photoluminescence data we found that the STVs decreased with increased laser fluence. (See Table 1) For the decay measurements, this is opposite to the trend expected from the Shockley-van Roosbroeck formulation for radiative decay rates in which lifetime decreases with increasing carrier concentration.³⁸ We attribute this effect largely to saturation of surface trap sites with additional contribution from surface screening. We have observed complimentary effects in the luminescence decay of GaAs in air before and after a surface treatment process known to remove surface species which trap minority carriers.⁵ In this case, the saturation effects become more pronounced as the number of surface traps is reduced by the process. That the surface traps can be saturated at moderate laser powers has important implications for the interpretation of experimental results. Clearly the power of the excitation must be carefully monitored and held constant when results under various experimental conditions are compared. These results also bear on the use of high injection radiative decay profiles in the determination of interfacial charge-transfer kinetics. The high injection condition is often employed in order to minimize effects due to space charge fields under open circuit conditions. According to our results, such studies will tend to underestimate surface trap state populations. It is notable that measurements of the STV performed on clean GaAs surfaces by others compare most favorably with the highest power results presented in our work where we believe that trap saturation is a factor.

(vi) *Photocorrosion :* Semiconductor/liquid junction solar cells are one of the more efficient means of conversion of solar radiation to electricity. However, their widespread use is hampered by photocorrosion, which limits their useful lifetime to an unacceptably

short period. The aim of the work described below is to better understand the corrosion process which is known to be accompanied by an increase in the minority carrier surface trapping velocity. In photoluminescence studies similar to those already described, photocorrosion of GaAs and the stabilizing effect of sulfide-containing electrolytes have been examined. We have found that corrosion can be induced at these interfaces if they are held in the depletion region and exposed to high power laser irradiation. The corrosion is accompanied by a drop in PL intensity at 1 V positive of flatband, and a corresponding increase in STV for decays taken positive of this voltage is observed. Figure 6 shows an initial photoluminescence versus voltage scan from a freshly prepared surface (solid line) and another scan taken after a total of three sweeps had been performed (dashed). The photon flux in this experiment was 7×10^{11} photons/(cm² pulse).

Figure 6. Photoluminescence from n-GaAs(100) in 0.25 M Na₂S; Incident power of 1×10^{12} photons/cm². The solid scan is the PL response initially. The dashed scan corresponds to the PL response after extended photolumination.

The drop in the photoluminescence signal at voltages > 0.0 V after three sweeps is long-lived and irreversible. This drop in count rate indicates that an additional nonradiative decay channel has opened near 0 V. PL decays taken from samples at various potentials before and after such exposure confirm that the drop in PL intensity is accompanied by an increase in the STV at potentials > 0.0 V. The voltage at which these traps begin to be accessed compares well with results of other workers who have determined the energy of corrosion induced traps by capacitance methods.^{39,40} We attribute this observed drop in photoluminescence to new surface states created in the photocorrosion process. Photocurrent measurements reveal that these corrosion induced traps are sites of radiationless electron-hole recombination and do not mediate charge transfer. Laser repetition studies indicate that the time to empty and refill the surface states on the uncorroded surface is on the order of microseconds and so these intrinsic traps likely mediate charge transfer.

Work is currently being performed on the comparison of photocorrosion on different crystallographic faces of GaAs. Preliminary results show that while the (110) and (100) faces are equally susceptible to photocorrosion, the resulting traps formed on the different faces are of a different nature.

(7) *Surface Passivation*:: A Na₂S coating on a chemically etched n-GaAs surface increases the observed PL intensity relative to an etched only sample⁴¹⁻⁴³. Such an increase in PL intensity has been explained by a reduction in trap density and/or unpinning of the Fermi energy level (removal of a depletion SCR)⁴¹. Yablonovitch and coworkers⁴⁴ determined the STV of n-GaAs in air before and after Na₂S coating by measuring the decay in n-GaAs conductivity after photogeneration of charge carriers. Numerous explanations have been given as to the effect of sulfide on the GaAs surface although not consensus has yet been reached. Our approach in these studies has been to resolve some of the outstanding issues of surface passivation by our STV measurement approach with particular focus on the effect of sulfide concentration on the creation the corrosion induced surface states discussed above. We have found that, for an electrode in highly concentrated (2 M) Na₂S, a longer laser exposure time is necessary to achieve corrosion than for an electrode in low concentration (0.008 M) of Na₂S. When corrosion does finally occur, it leads to traps that can be accessed at all voltages, not only at V > 0.0 V. Because the increased concentration of Na₂S does not affect the energetic position or density of mid-gap states, and because the photocurrent is significantly higher, the increased protection from photocorrosion is attributed to a higher rate of charge transfer to solution and a lower rate of corrosion.

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2. Research Publications, Presentations and Related Activities

a. DOE Supported Research Publications

- (1) "Power Dependent Effects in Photoluminescence vs. Voltage Scans of GaAs/Electrolyte Junctions Using Picosecond Pulse Excitation", J.F. Kauffman, B.A. Balko and G.L. Richmond, *J. Phys. Chem.*, 96 (6371) 1992.
- (2) "Power Dependent Effects in the Luminescence Decay of GaAs/Electrolyte Contacts at the Flat Band Potential", J.F. Kauffman, B.A. Balko and G.L. Richmond, *J. Phys. Chem.*, 96, (6374), 1992.
- (3) "Dependence of Luminescence Decays from GaAs/Electrolyte Contacts on Excitation Power and Applied Bias: Examination of the Modified Dead Layer Model", J. F. Kauffman and G. L. Richmond, *J. Appl. Phys.*, 73 (1993) 1912.
- (4) "Corrosion Induced Surface States on GaAs Electrode Surfaces as Studied by Picosecond Luminescence Measurements", B. Balko, J. Kauffman and G.L. Richmond, *J. Phys. Chem.*, 97 (9002) 1993.
- (5) "Sensitivity of Second Harmonic Generation to Space Charge Effects at the Si(111)/Electrolyte and Si(111)/SiO₂/Electrolyte Interfaces", P. R. Fischer, J.L. Daschbach, D.E. Gragson and G.L. Richmond, *J. Vac. Sci. and Tech.*, 12, 2617 (1994).

- (6) "Picosecond Photoluminescence Studies of Recombination Dynamics at n-GaAs/Electrolyte Interfaces, G.L. Richmond, J. Kauffman and B.A. Balko, Surface Imaging and Visualization, CRC Press, A.T. Hubbard, Ed., in press.
- (7) "Passivation and Stabilization of GaAs Surfaces by Sulfide Containing Solutions", B. A. Balko, E. A. Miller and G.L. Richmond, *J. Phys. Chem.*, in press.
- (8) "Observation of the Potential Dependent Second Harmonic Response from the Si(111)/Electrolyte and Si(111)/SiO₂/Electrolyte Interfacial Region", J.L. Daschbach, P. R. Fischer, D.E. Gragson, D. Demarest and G.L. Richmond, *J. Phys. Chem.*, 99, 3240 (1995).in press.
- (9) "Photoluminescence Studies of Porous Silicon", R. Swischer, P. Sercel and G.L. Richmond, *J. Chem. Ed.*, in press.
- (10) "Optical Studies of n-GaAs by Time Correlated Single Photon Counting Techniques", E. Miller and G.L. Richmond, *Proceedings of the Japan/NSF Joint Workshop of Photo-induced Processes at Semiconductor Electrochemical Systems*, in press.

b. Invited Talks on the Research Supported by DOE:

"Photoinduced Processes at Semiconductor Surfaces", NSF Sponsored Joint US-Japan Workshop on Semiconductor Photoelectrochemistry, La Jolla, CA, March 1995.

"Photoinduced Processes at n-GaAs/Electrolyte Interfaces", Phillips Lectureship at Haverford College, Haverford, PA, February 1995

"Surface Second Harmonic Generation Studies of Electrode/Electrolyte Interfaces", Surface Studies by Nonlinear Optical Spectroscopies, Kassel, Germany, May 1994.

"Nonlinear Optical Studies of Surfaces and Interfaces", American Vacuum Society Meeting, Seattle, WA, November 1993.

"Electrode/Electrolyte Interactions as Probed by Nonlinear Optical Methods", 206th National American Chemical Society, Chicago, Ill, August 1993.

"Picosecond Studies of Photoinduced Processes at N-GaAs/Electrolyte Interfaces" International Laser Science/Optical Science Association Meeting, Toronto, October 1993.

"Surface Science Under Water: Probing the GaAs/Electrolyte Interface", Gordon Research Conference on Analytical Chemistry, August 1993.

"Surface Science Under Water", Iota Sigma Pi Convention, Cleveland, OH, , June 1993.

"Surface Science Under Water", Department of Education Fellowship Workshop, University of Southern California, February 1993.

"Pulsed Laser Studies of Electrode/Electrolyte Interfaces", Deutsche Bunsengesellschaft fur Physikalische Chemie, Mainz, Germany, Oct. 1992.

"Nonlinear Optical Studies of Surfaces and Interfaces", 204th National American Chemical Society Meeting, Washington, DC, Aug. 1992.

d. Contributed Talks on Research Support by DOE

"Wavelength Dependent Studies of the SH Response from Si/Electrolyte Interfaces", P. Fischer and G.L. Richmond, American Physical Society Meeting, San Jose, CA, March 1995.

"Comparative Studies of the Photoluminescence Behavior (110) and (100) Faces of n-GaAs", E.A. Miller and G.L. Richmond, American Physical Society Meeting, San Jose, CA, March 1995.

"SHG Studies of Si/Electrolyte and Si/SiO₂/Electrolyte Interfaces", P. Fischer and G.L. Richmond, Electrochemistry Gordon Research Conference, Ventura, CA, January 1995.

"Second Harmonic Generation Studies of Si/Electrolyte and Si/SiO₂ Electrolyte Interfaces", P. Fischer and G.L. Richmond, American Chemical Society Meeting, Washington, DC, August 1994.

"Si(111)/SiO₂ Interface Probed by Optical Second Harmonic Generation in UHV", D. Gragson and G.L. Richmond, Western Spectroscopy Conference, Asilomar, CA, January 1994.

"Photoluminescence Studies of GaAs Electrode Surfaces", E. Miller and G.L. Richmond, Department of Education (GAAN) Symposium, Charleston, OR, June 1994.

"Sensitivity of Second Harmonic Generation to Space Charge Effects at the Si(111)/Electrolyte and Si(111)/SiO₂/Electrolyte Interfacial Regions", P.R. Fischer, J.L. Daschbach and G.L. Richmond, Western Spectroscopy Association, Asilomar, CA, January 1994.

"Observation of the Potential Dependent Second Harmonic Response from the Si(111)/Electrolyte and Si(111)/SiO₂/Electrolyte Interfaces", Department of Education, GAANN Symposium, Charleston, OR, June 1994.

"Si(111)/SiO₂ Interface Probed by Optical SHG in UHV", D. Gragson and G.L. Richmond, Western Spectroscopy Conference, Department of Education, GAANN Symposium, Charleston, OR, June 1994.

"Studies of the Si/SiO₂/Electrolyte Interface by SHG", P. Fischer, J. Daschbach and G.L. Richmond, American Chemical Society Meeting, Denver, CO, March 1993.

"Nonlinear Optical Studies of n-Si(111) Surfaces in Electrolyte Solutions", P.R. Fischer and G.L. Richmond, 40th Western Spectroscopy Association Meeting, Asilomar, CA, January 1993.

"Photoluminescence Studies of GaAs Electrode Surfaces", B. Balko, E. Miller and G.L. Richmond, 40th Western Spectroscopy Association Meeting, Asilomar, CA, Jan. 1993.

"Nonlinear Optical Studies of n-Si(111) Surfaces in Electrolyte Solutions", P.R. Fischer, J.L. Daschbach and G.L. Richmond, Chemical Physics Institute Retreat, Charleston, OR, September 1993.

"Si(111)/SiO₂ Interface Probed by Optical SHG in UHV", D. Gragson and G.L. Richmond, Chemical Physics Institute Retreat, Coos Bay, OR, September 1993.

e. Awards and Honors awarded to the PI during the funding period:

American Physical Society Fellow Award 1993

Agnes Faye Morgan Research Award (Iota Sigma Pi) 1993