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A2. PROGRESS FROM THIRD YEAR OF DOE FUNDING

Title: Monitoring Interfacial Dynamics by Pulsed Laser Techniques
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The goal of the DOE sponsored studies in this laboratory has been the development and application of new optical methods to the study of dynamic processes at the electrode/electrolyte interface. The double layer processes of interest include the electrodeposition of thin films, adsorption and desorption of ions and molecules at the surface, surface reconstruction, carrier dynamics in photo-excited materials, and photo-induced electron transfer. In the past year we have used optical second harmonic generation (SHG) for time resolved measurements of thallium deposition on Cu(111). The studies of carrier dynamics in photo-excited materials have involved both steady state and picosecond time-resolved luminescence measurements following photoexcitation of the semiconductor material. The progress made since our last annual report made is outlined below.

1. Photoinduced Effects at Semiconductor Electrode Materials

a. Photowashing of GaAs

The first study has focussed on elucidating the photochemistry responsible for a GaAs surface treatment process known as photowashing. Photowashing is a process whereby the concentration of surface impurities on GaAs is photochemically reduced. These impurities impede ones ability to adjust interfacial energetics with an external potential, and thus hamper efforts to construct useful surface barrier devices with GaAs. *To date a comprehensive study of the chemistry responsible for surface quality improvements due to photowashing is lacking.* We have addressed this issue by developing an experimental apparatus which allows us to observe photoluminescence from GaAs as a function of time as it is being photowashed.

Photoluminescence intensity is quite sensitive to surface quality, and thus provides a convenient method for monitoring the extent of surface quality improvement during photowashing. By adjusting experimental parameters and observing their influence on the time-dependent photoluminescence intensity during photowashing, we have begun to elucidate important mechanistic information about the photowashing process. We have shown conclusively that surface quality improvement occurs during the photowashing process, and does not require the activation step following treatment

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which other researchers observe. We have learned that oxide removal by water washing alone prior to photowashing can accelerate the rate of surface quality improvement during photowashing. We have also observed that improvements in surface quality can be maintained for extended periods while photowashing is continued. This result is in direct contrast to many previous studies in which photoluminescence measurements were made only before and after photowashing, and has important implications for the use of photowashing in multi-step surface passivation procedures. In addition to these measurements, which are carried out with time resolution in the microsecond and longer regime, we have measured luminescence decay profiles following picosecond optical excitation by the time correlated single photon counting method. These measurements allow us to observe the decay of luminescence following short pulse excitation with picosecond time resolution. By making such measurements before, during and after photowashing GaAs, we can gain more detailed information into the physical mechanisms responsible for photoluminescence enhancement. Our results indicate that charge separation and surface trapping are both equally important non-radiative decay mechanisms in untreated samples, while surface trapping dominates the non-radiative decay of photowashed GaAs. Furthermore, following photowashing the surface trap state density has been sufficiently reduced so that saturation of the traps can be accomplished with modest laser power densities. Surface recombination velocities measured from these decays also help to quantify the improvement in surface quality. (Ref. 3 in publication list below)

b. Picosecond Studies of Photoelectrochemical Processes

The second and most recent experiments has focussed on the study of picosecond time resolved luminescence decays from GaAs in electrochemical environments. In particular, we are interested in developing an understanding of the carrier dynamics which occur following photo-excitation of the n-GaAs(100)/electrolyte interface. We have gathered a wide range of data on this system which we have organized into two different publications. (Ref. 4 and 5 in publications list below). The findings from these studies are outlined below.

The first study has examined power dependent effects in the luminescence decays at the GaAs/electrolyte interface biased at the flat band potential. We have found that even under laser excitation with moderate power, there is a strong power dependence in the temporal response. Figure 1 shows decays from a GaAs electrode measured at three

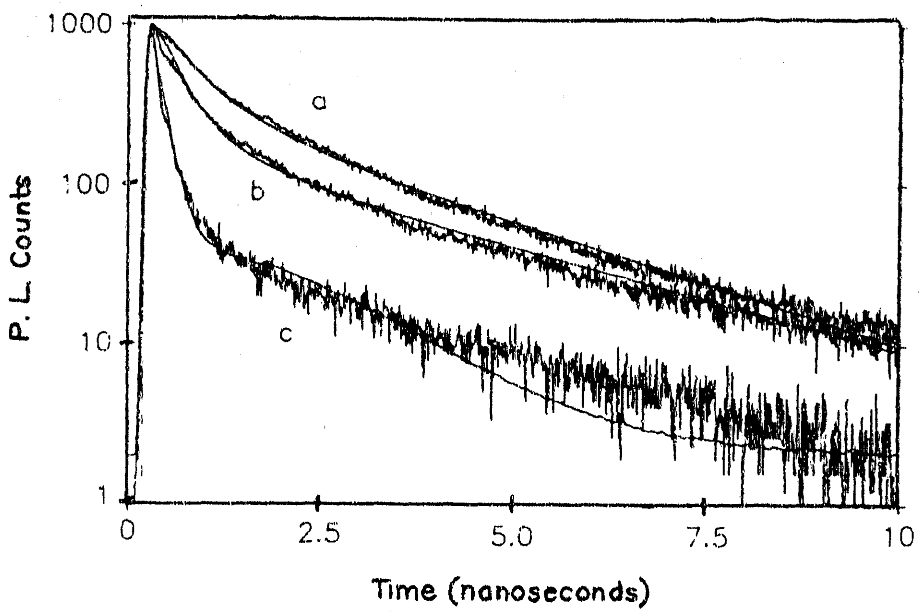

Figure 1. Fluorescence decays (855 nm) from n-GaAs(100) in 0.1 M KOH/0.1 M Na_2S/0.01 M S (pH=13, V=-0.63 vs Ag/AgCl). Excitation was with 532 nm pulses of 5psec duration. The three excitation fluxes are (a) 4 x 10^{12}; (b) 1 x 10^{12}; (c) 3 x 10^{11} photons/cm^2/pulse. The fits to the data have been modelled as described in the text.

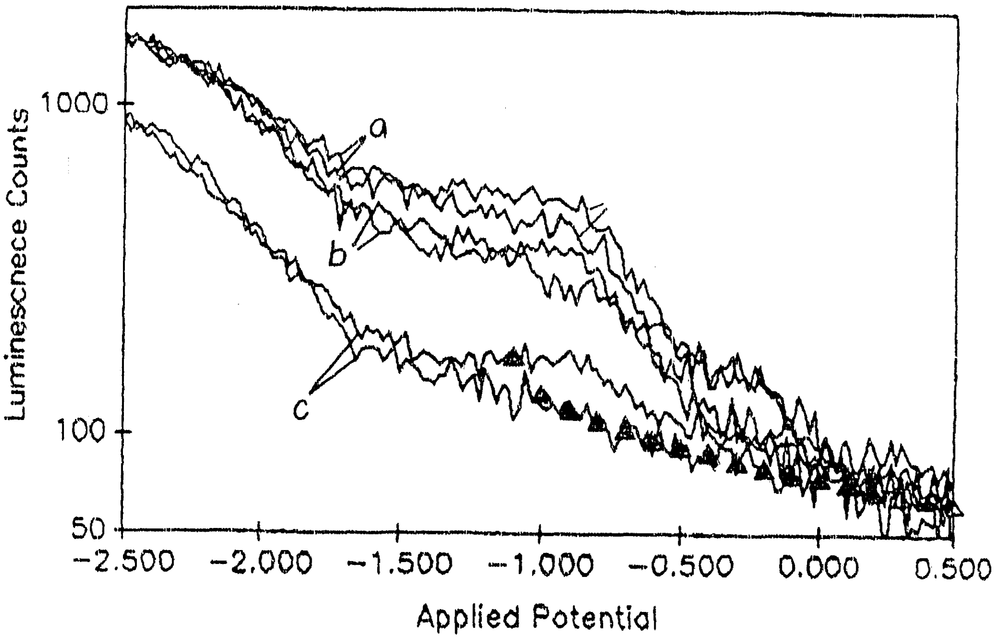

Figure 2. Potential dependence of fluorescence (855 nm) from n-GaAs(100) in 0.1 M KOH/0.1 M Na_2S/0.01 M S (pH=13, V vs Ag/AgCl). Excitation was with 532 nm pulses of 5psec duration. (a) 1.7 W/cm^2; (b) 0.44 W/cm^2; (c) 0.11 W/cm^2; (d) HeNe laser excitation with 1.4 W/cm^2.

excitation power levels. The decays are highly non-exponential at early times, but asymptotically approach exponential behavior near the end of the observation time. We observe a trend toward longer decays as power is increased. This longer decay reflects both a decrease of the initial slope of the decay, as well as an increase in the portion of light which occurs at long times following excitation. 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. We have attributed these effects to saturation of surface trap states which cause the surface recombination velocity to vary with excitation power and to also change with time following excitation. We have developed a model to describe the data which is an extension of previous models used to describe surface minority trapping rates. Our addition has been to represent the cross section for minority trapping as an activated process rather than one which is constant throughout the decay. Thus as the trap sites of low activation are barrier are preferentially filled, the effective barrier with increase, giving rise to a time varying surface recombination velocity. Without this time varying surface recombination velocity, we find that we can not adequately model the curvature observed in our data. Figure 1 shows our fit to the data using this model. We also find that we can then extract a value for the surface non-radiative rate constant at time t=0 from the initial slope of the luminescence decay. The results of these studies have important implications for use of high injection radiative decay profiles in the determination of interfacial charge transfer kinetics. The high injection condition has generally been employed in previous studies to minimize effects of the space charge fields under open circuit conditions. According to our results such studies can give useful information regarding the surface trap state population, but cannot be used to extract meaningful charge transfer rates without additional independent evidence which corroborates that carrier trapping is the rate limiting step.

In the second study we have been investigating these power dependent effects in photoluminescence as the voltage is varied across the GaAs/electrolyte interface. The data is analyzed with a modified dead layer model, which allows the determination of surface and bulk parameters of the semiconductor/electrolyte system. Figure 2 shows the potential dependence of the photoluminescence as the bias voltage is varied from 0.5 to -2.5 V under picosecond illumination at three different laser intensities. The potential range encompasses the behavior from inversion to accumulation conditions. All scans using pulsed excitation show an increase in luminescence intensity as the bias voltage is adjusted from the depletion condition to the flat band condition, consistent with the dead layer model. The dramatic increase in overall intensity as the laser power is increased is attributed to the saturation of fast surface traps as described above. Each scan also exhibits a dramatic improvement in luminescence intensity in the accumulation region, which we attribute to reduction of the effective surface recombination velocity due to the repulsion of minority carriers from the surface. Also depicted is the potential dependence of the luminescence under cw HeNe excitation. As with the picosecond scans, there is an overall increase in intensity in the accumulation region relative to the depletion region. However, as the flat band conditions are approached, the HeNe laser scan exhibits no enhanced luminescence beyond that predicted by the dead layer model even though the average laser power is comparable to that of the highest power picosecond excitation scan. We believe that this is evidence that the observed power dependence is due to the saturation of fast surface states. The luminescence intensities obtained in the depletion to flat band region are found to be well fit by the modified dead layer model. Beyond -1.0 V, disagreement is found as would be expected since the model does not address the occurrence of recombination currents which occur beyond this potential. By comparing the calculated intensity with the experimental results obtained using higher laser powers, we are able to extract values for the surface minority trapping rate from the data.

2. Dynamics at Metal Electrode Surfaces

Over the past several years we have been investigating the kinetics of potential induced phenomena in metal/aqueous electrode systems by time resolved SHG. SHG offers several advantages for such studies including the inherent surface sensitivity of this nonlinear optical process, the ability to access interfaces between two dense media and the applicability to study of dynamic processes over a wide range of timescales. The experiments described below are unique to this laboratory. They have involved the application of a fast potential step to the surface. The potential induced changes at the surface are then monitored via the SH response from a mode-locked 80 MHz Nd:YAG laser which acts as a "continuous" probe of the surface following the perturbation. (Ref. 2 and 6 below)

During the past year we have been involved in monitoring the kinetics of electrodeposition of thallium on Cu(111). The experiments are somewhat more complicated than our previous polycrystalline Ag studies described in that they take advantage of the variation in the SH response as the single crystal electrode surface is rotated azimuthally by 360°. For a Cu(111) surface of three fold symmetry, we find that the SH response gives three maxima and minima, consistent with the C_{3v} symmetry of the surface region. The time-resolved measurements then involve measuring the rotational anisotropy at various stages of deposition, followed by monitoring the time evolution of the deposition at a fixed rotation angle. By judicious choice of the rotation angle, one can isolate the SH response corresponding to various surface response features. For example, when one uses p-polarized incident light and monitors the p-polarized SH response, and fixing the azimuthal angle of 30°, one can monitor the temporal response from the out-of-plane (isotropic) response from the surface. With p-input and s-output polarization and an azimuthal angle of 30°, one can monitor the in-plane (anisotropic) response.

Careful comparative studies of the rotational anisotropic SH response of Cu(111) in UHV and *in situ* have shown that a surface oxygen containing species is present on Cu(111) electrodes in solution near - 0.2 V. The oxide species is electrochemically reduced near -0.6 V and is therefore present during monolayer thallium deposition at a more anodic potential in the experiments described here. The SH intensity and the relative phase angle between the isotropic and anisotropic response of the native Cu(111) electrode are sensitive to the oxide. With oxygen dosing, the SH intensity at 0 degrees decreases and the phase angle increases. The observed SH pattern shifts from six maxima and minima to three maxima and minima, as was previously reported for Cu(111) in air. One of the most interesting results of our preliminary data analysis for thallium deposition on Cu(111) electrodes is that the type of deposition kinetics observed appears to depend on how much oxygen containing species is present on the electrode. Secondly, the time resolved anisotropic and isotropic responses are quite different for the same electrode surface preparation

The results for the time-resolved measurements of deposition of one ML thallium on Cu(111) following a potential step from -0.20 V to -0.55 V are shown in Figures 3 and 4. The plane of incidence of the 1064 nm laser beam is fixed at 30 degrees with respect to the [211] crystal direction. For the experiments shown in Figure 3, the presence of the oxygen containing species was minimized by refined electropolishing and oxygen exclusion procedures. The SH rotational anisotropy pattern at -0.2 V for the electrode in Figure 4 suggests a greater coverage of oxide. Figures 3(a) and 3(b) show The corresponding time dependent anisotropic contributions for the respective surface preparations.

Following the initial rapid fall in the SH response due to double layer reorganizations, the isotropic SH response $I_{p,p}(t)$ from the less oxidized Cu(111) electrode decreased linearly with time as the first thallium monolayer was deposited (Figure 3(a)). The electrochemical cell current transients obtained simultaneously show the same temporal behavior. The observed linear relationship suggests that deposition on

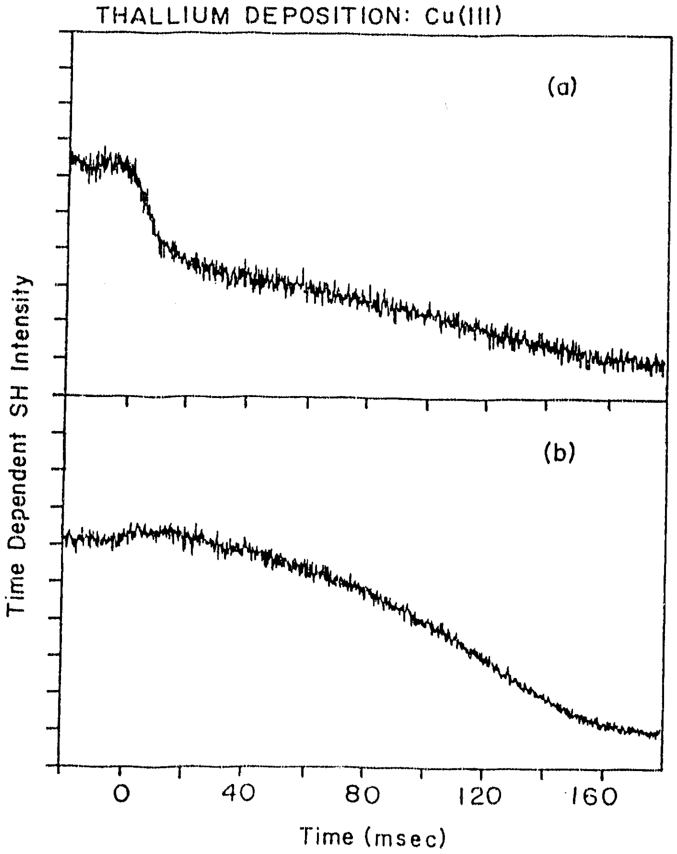

Figure 3. Transient SH response of a Cu(111) electrode during thallium underpotential deposition (1 ML). Incident wavelength = 1064 nm. (a) Isotropic SH signal, $I_{p,p}(t)$. (b) Anisotropic SH signal, $I_{p,s}(t)$.

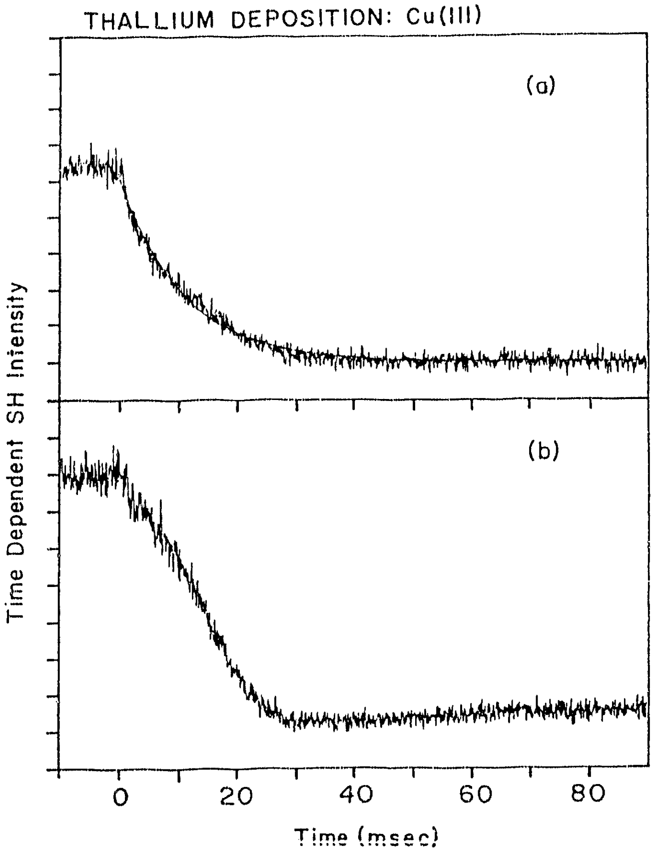

Figure 4. See text.

this Cu(111) surface occurs by a nucleation mechanism, not by an absorption (exponential) or diffusion controlled ($t^{-1/2}$) process. Figure 3(b) illustrates that the transient anisotropic response of the Cu(111) surface is different from the isotropic response. A slight initial increase in $I_{p,s}(t)$ occurs during double layer reorganization. The subsequent transient decay of the anisotropic SH signal is not linear. The data may indicate that the rate of deposition, i.e. the rate determining step, is direction dependent.

Both the isotropic and the anisotropic components of $\chi^{(2)}$ initially decrease and reach a minimum near 30 msec. Although both SH transients fall to a minimum at about the same time, their form is quite different and qualitative comparisons are useful. The isotropic contribution, $I_{p,p}(t)$, decays as a single exponential with a decay of $\tau = 10.7$ msec. The exponential form suggests that the deposition occurs by an adsorption, rather than a nucleation, mechanism. The transient anisotropic response is not as simple. In fact, the initial fall in $I_{p,s}(t)$ is not a simple decaying exponential. The differing time dependences for the isotropic and anisotropic responses suggests that ζ, the bulk anisotropic susceptibility element which is the only common element, is not the main source of the nonlinear response in either case.

We have also found that the time constant for adsorption of the first thallium overlayer depends on the final potential, E_f, of the potential step. We investigated the effect of underpotential and overpotential steps on the best fit values of τ for exponential fits to $I_{p,p}(t)$. The under- and overpotentials, ΔE, are defined with respect to the maximum of the current peak, E_p, in the CVs for the first monolayer deposition. The time required to form the deposit increases at anodic potentials ($\Delta E<0$) closest to E_p, indicating that more time is required to deposit successively larger coverages. The form of the data suggests that τ would reach a maximum near $\Delta E=0$. In the overpotential region, where the final coverage should be independent of E_f, the overlayer is formed faster as the overpotential increases. This result suggests that activation energy is supplied by the overpotential. Similar results were reported in related SHG measurements of the UPD kinetics of thallium deposition on polycrystalline electrodes within the overpotential region.

3. Summary of Research Activity for the past year

a. Publications on the Research Supported by DOE

(1) "Investigations of Electrochemical Interfaces by Nonlinear Optical Methods", G. L. Richmond, In-situ Studies of Electrochemical Interfaces, H. Abruna, ed., VCH Verlag Chemical, 1991.

(2) "Second Harmonic Generation and Surface Structure of Electrodes" invited review article for Advances in Electrochemical Science and Engineering", H. Gerischer and C.W. Tobias, ed., VCH Publishers, 1991.

(3) "Picosecond Studies of Photowashing on GaAs", J. Kauffman and G.L. Richmond, Appl. Physics, 59, (561) 1991.

(4) "Power Dependent Effects in the Luminescence Decay of GaAs Electrolyte Contacts at the Flat Band Potential", J.Kauffman and G.L. Richmond, submitted.

(5) "Power Dependent Effects in Photoluminescence from the GaAs/Electrolyte Junctions Using Picosecond Pulse Excitation", J. Kauffman and G.L. Richmond, submitted.

(6) "Kinetics of Deposition of Thallium on Cu(111) by Optical Second Harmonic Generation", J.M. Robinson and G.L. Richmond, in preparation.

b. Invited Research Talks on the Research Supported by DOE

18th Annual FACSS Meeting, Anaheim, CA, "Comparison of Surface Properties in Solution and in UHV by Second Harmonic Generation", October 1991.

178th National Meeting of the Electrochemical Society, Phoenix, AZ, "What CAn SHG Tell Us About Surface Atomic and Electronic Structure of Metal Surfaces", October, 1991.

NSTA National Meeting, Shell Lecture, "Lasers in Chemistry", Houston, TX, March 1991.

Gordon Research Conference on Electrochemistry, "Surface Science Under Water", January 1991, Ventura, CA.

Additional invited seminars on the DOE research have been given at the following:
IBM Almaden Research Laboratories, San Jose, CA, June 1991.
University of Arizona, Tucson, AZ, April 1991.
University of Utah, Salt Lake City, UT, April 1991.
University of Toronto, Toronto, Canada, April 1991.
Oberlin College, Oberlin, OH, April 1991.
Pomona College, Los Angeles, CA, February 1991.

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