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MONITORING INTERFACIAL DYNAMICS BY PULSED LASER TECHNIQUES

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ANNUAL REPORT

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Our investigation of interfacial dynamics has progressed well during the first year of DOE support. We have surveyed several types of materials including thin film and layered semiconductors as well as a metal and semimetal. We have made new second harmonic(SH) generation measurements on these materials using both nanosecond(Q-switched) and picosecond(mode-locked) pulsed Nd:YAG lasers with appropriate gated or photon counting detection. Many of our initial studies have been performed under steady state conditions in order to optimize the experiments for time-resolved studies. Moreover, we have recently been successful in extending SHG to the time domain. With regards to new directions beyond the initial ones proposed, we have recently developed a means of monitoring surface structure and reconstruction phenomena in-situ. This discovery now opens a broad new area of dynamic interfacial measurements to be done in-situ.

1. SH Characteristics of Photoactive Materials

The transition metal dichalcogenides are narrow bandgap semiconductors whose photophysical properties make them attractive photocell candidates. Examples include $MoSe_2$, WSe_2 and SnS_2. One advantage of these materials is that they do not require extensive surface preparation. An oxide free single crystal surface is prepared by simple cleavage between layers. We have found, however, that laser fluence must be carefully controlled because the damage threshold of these materials is low. We have observed strong, stable reproducible SH signals from the dichalcogenides in air and in-situ using the nanosecond Nd:YAG laser. Furthermore, there is no evidence of background luminescence, a factor which is very important for our proposed studies. The SH observed from these materials is independent of applied dc potential from -200 mV to +800 mV (vs. Ag/AgCl). Conversely, the SH signal from the new semimetal WTe_2 in-situ increased dramatically over this range. The potential dependence may be related to an oxide which forms on the surface unless cleaved in vacuum. In the coming year, we plan to use SHG as a probe of interfacial dynamics of the dichalcogenides in response to a photopulse of sufficient energy to create electron-hole pairs. Critical to the progress of these experiments is the acquisition of a new laser system which will allow us to extend our current capabilities from the nanosecond range into the picosecond and femtosecond time scales where a larger proportion of the interesting electron transfer processes will likely occur. Anticipating this possibility, we submitted a proposal(# 8702-114) for a femtosecond laser system to the University Research Instrumentation and are awaiting a decision.

Preliminary static measurements of SH from the thin film semiconductor amorphous selenium (on a quartz substrate) have now been completed. Amorphous selenium is a highly nonlinear optical material whose photoresponse in the visible region is of technological interest. We readily observe SH signals from these samples using 100 psec, 1.06 μm laser pulses and photon counting equipment. There is a strong dependence of SH intensity on film thickness, an additional effect which we have investigated. Attempts to monitor SH from thin films of tellurium, which has a still larger nonlinear susceptibility, were thwarted by melting of the film even at the lowest laser fluence.

DISCLAIMER

2. Time Resolved Measurements

We are developing SHG as a real time probe of dynamics at the solid/liquid and solid/air interface. Our approach uses SHG to monitor the response of the system at a known time delay following a perturbation such as an applied voltage pulse or a laser pulse which causes a thermal or photoexcitation. In our first successful experiments in this area, we have studied the time dependence of the charging of a polycrystalline silver surface in Na_2SO_4. The electrochemical double layer is first perturbed by a dc voltage pulse of short duration. A 1.06 micron, 10 ns pulse from an externally controlled Nd:YAG laser then strikes the sample at a known delay with respect to the voltage step. By monitoring the SH light generated by the IR laser pulse at numerous delays, we have captured the complete transient response of the restructuring of the double layer after the perturbation. One drawback to our current operation is that it takes several hours to capture a single decay curve since each delay point requires signal averaging at a repetition rate of 0.3 Hz. The solution to this situation is to use the 76 MHz, 100 psec YAG laser with photon counting equipment which will enable us to "continuously" monitor the SH response to the applied voltage step. We are currently assembling the equipment for these experiments.

One of the most exciting results in our laboratory which was not anticipated at the time of the initial application of this grant is our ability to use SHG to measure surface reconstruction phenomena. By exploiting the rich polarization dependent properties of SHG, we have developed a means of monitoring surface structure of single crystal electrodes in-situ. We find that the surface order is highly dependent on a number of factors including supporting electrolyte and potential application. Important to this DOE supported project is the time dependence that we have observed in surface reconstruction phenomena. This now opens a wide field of possibilities for us to study in a time-resolved mode. Such studies include the dynamics of potential and temperature induced reconstruction, the kinetics of ordered film growth on electrode substrates and the rates of adsorbate reorientation.

B. Research Plans for the Second Year of DOE Funding

Many of the experiments planned for the coming year are a continuation of the studies from the previous year. To reiterate on the studies mentioned above, we will continue to focus on determining rates of various potential, photo and thermal induced processes at the solid/liquid junction.

The experiments involving an applied dc voltage perturbation will continue and will primarily investigate noble metals and silicon. Two types of experiments will be done. The first experiments will be aimed at correlating the SH response from a polycrystalline silver electrode surface with the measured electrostatics of the interface. A second set of experiments will focus on reconstruction phenomena on silver and gold single crystals. We intend to investigate the rates of changes in surface order of single crystal electrodes after application of a fast potential step of varying characteristics. We have evidence that this phenomena is mediated by the electrolyte. Hence, these rates will be studied as a function of electrolytic solution. In related studies, we will investigate the rates and patterns of metals reduced on the surface of the electrode by

underpotential deposition. If time permits, we will investigate reconstruction phenomena following a fast thermal perturbation.

The potential dependent phenomena described in the last paragraph should be accessible with the 10 nanosecond time resolution afforded by our available equipment. However, the response of a metal or semiconductor to an optical perturbation is expected to be much faster. With these photoactive electrode materials our intention is to investigate the rates of photo-induced electron transfer using SHG in optical/optical pump/probe experiments both in-situ and ex-situ. We are planning to start with the dicalcogenides $MoSe_2$, WSe_2 and SnS_2 which have bandgaps in the visible region. Using a recently acquired YAG laser which gives us 100 psec resolution, we will be measuring the transient SH response of the material after the photoexcitation. In addition to this laser being useful as a continuous monitor of processes on longer time scales, it will also be adequate for very slow charge transfer events in the nanosecond and subnanosecond regime. However, it is clear from recent measurements that many events involving charged carriers occur on faster timescales which would only be accessible with the femtosecond system which has been requested from DOE(URIP). There is currently so little known about the rates of photo-induced electron transfer in this time regime that the studies should have a significant impact on this field.

Important to the studies of photoactive materials is the optical characterization of the semiconductor electrodes with respect to bandgap and surface state energies. These measurements are critical to our investigations to both enhance our SH signals and to aid in the choice of an appropriate excitation wavelength. As a result, we are currently constructing a photothermal deflection station which will allow us to make optical measurements of these parameters and use this data in the SHG studies. This effort will also continue during the next year.

C. Summary of Research Activity (Aug. 1, 1986 - July 31, 1987)

1. Publications on the Research Supported by DOE

"Nonlinear Optical Studies of Semiconductor Interfacial Properties", J. M. Robinson and G. L. Richmond, Advances in Laser Science - II, M. Lapp and G. A. Kenney-Wallace, eds. (Am. Inst. of Physics, NY 1987), in press.

"Monitoring Surface Structure and Interfacial Properties via Second Harmonic Generation", J. M. Robinson, H. M. Rojhantalab, V. L. Shannon, D. A. Koos and G. L. Richmond, IUPAC Journal of Pure and Applied Chemistry, in press.

"Static and Time-Resolved Nonlinear Optical Studies of Semiconductor Interfacial Properties", J. M. Robinson and G. L. Richmond, Proceedings of the Tenth International Conference on Raman Spectroscopy, Eugene, OR, Eds. W. L. Peticolas and B. Hudson, 1986, chapt. 5, p. 66.

"Second Harmonic Generation Studies of Interfacial Structure and Dynamics", G. L. Richmond, invited review paper for Progress in Surface Science reporting on the topics supported by this grant.

2. Talks on the Research Supported by DOE(Aug. 1, 1986 - July 31,1987)

Chemically Modified Surfaces Symposium, Ft. Collins, CO, "In-Situ Characterization of Interfacial Phenomena", June 1987.

Electrochemical Society Meeting, Philadelphia, PA "In-Situ Characterization of Solid/Liquid Interfaces by Optical Second Harmonic Generation", May 1987.

13th Annual FACSS Meeting, St. Louis, MO "Nonlinear Optical Studies of Electrochemical Interfaces", September 1986.

Gordon Research Conference on Electrochemistry, Santa Barbara, CA "In-Situ Measurements of Surface Ordering on Single Crystal Electrode Surfaces by Optical Second Harmonic Generation", January 1987.

193rd ACS National Meeting, Denver, CO, "In-Situ Measurements of Surface Order of Single Crystal Electrodes by Second Harmonic Generation", April 1987.

Northwest Regional ACS Meeting, Bellington, WA, "In-Situ Characterization of Single Crystal Electrode Surfaces by Optical Second Harmonic Generation", June 1987. (Given by post-doctoral fellow Victoria Shannon)

Additional invited seminars have been given at the following:

University of Illinois, Department of Chemistry, Urbana, IL, November 1986.

University of Washington, Department of Chemistry, Seattle, WA, October 1986.

Bringham Young University, Department of Chemistry, Provo, Utah, January 1987.

IBM Almaden Research Laboratories, San Jose, California, March 1987.

Stanford Research Institute, Palo Alto, California, March 1987.

Standard Oil Research Laboratories, Cleveland, Ohio, April 1987.

University of Virginia, Department of Chemistry, Charlottesville, VA, April 1987.

Portland State University, Department of Chemistry, Portland, OR, May 1987.

University of California, Department of Chemistry, Riverside, CA, May 1987.

3. Poster Presentations on the Research Supported by DOE(Aug. 1, 1986 - July 31,1987

ILS/OSA International Laser Science Conference, Seattle, WA, J. M. Robinson and G. L. Richmond, "Nonlinear Optical Measurements of Semiconductor Interfacial Kinetics", October 1986.

Xth International Conference on Raman Spectroscopy, Eugene, OR, J. M. Robinson and G. L. Richmond, "Static and Time-Resolved Nonlinear Optical Studies of Semiconductor Interfacial Properties", September 1986.