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Use of *in situ* Scanning Tunneling Microscopy for the Study of Dye Sensitization of Semiconductor Electrodes

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by

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We have made substantial progress on the goals set out in the initial proposal. We started out three years ago with an empty lab and no personnel trained in photoelectrochemistry. In the three years we have set up a state-of-the-art computer-controlled photoelectrochemical characterization laboratory with facilities to measure Mott-Schottky behavior, photocurrent spectra and photocurrent voltage curves on semiconductor electrodes. We have also set up a Bridgeman crystal growth furnace for preparing our own single crystals of SnS_2 and other semiconductor materials for our photoelectrochemical studies. The first boules of SnS_2 have recently been prepared. We have also modified a scanning tunneling microscope to perform photo-STM experiments to spatially resolve photocurrents on semiconductor surfaces. Progress in this area will be discussed later in this report.

Perhaps more importantly we have now a core of students who are well trained in photoelectrochemical and scanning probe techniques. In addition a post-doctoral fellow, Henning Sirringhaus, will be joining the group in October 1995. Dr. Sirringhaus has extensive training in both scanning probe techniques and photoelectrochemistry. We anticipate his expertise will allow us to increase the resolution and signal to noise in the photo-STM experiment to detect single chromophores. In addition, the acquisition of a Ti:sapphire laser system from the DOE-URI program will give us the power and flexibility in the light source to provide a better chance of single molecule detection. These ideas are further developed in the body of the renewal proposal.

Many of the details of our results on sensitization can be found in the attached preprints but the results will be summarized below. Dye sensitization of the single-crystal n-type semiconductor, SnS_2 , with both methylene blue (MB^+)

and cresyl violet (CrV^+) was studied. The quantum yield for sensitized photocurrent was found to depend on the condition of the SnS_2 surface. A higher sensitization yield is obtained near step edges and defects on the crystal surface and no sensitization is observed for CrV^+ on a nearly perfect surface unlike MB^+ where sensitization still occurs on nearly perfect surfaces. Intercalation of dye molecules in exfoliated areas of the crystal and the proximity of dye molecules to surface defects may both be responsible for the higher yields. Analysis of the MB^+ adsorption data on a smooth surface, with a Langmuir isotherm, indicates that the dye molecules are lying flat on the surface. When the two dyes are coadsorbed on the electrode, in the absence of a reducing agent, MB^+ can be selectively photooxidized from the surface with either 689 nm light (near the methylene blue absorption max) or 632.8 nm light (near the cresyl violet absorption max). This selectivity is explained by the much faster adsorption/desorption kinetics for cresyl violet allowing for the replenishing of the photooxidized dye on the time scale of the experiment. A model for dye sensitization in this system is proposed where a majority of adsorbed dyes act as antennae while a few at special sites are efficient at electron injection.

The effect of chemically and photoelectrochemically etching the surface of n- SnS_2 photoanodes on the dye sensitized photocurrent was investigated. For the photoetching process the effect of etching time and etching electrolyte was investigated with various above bandgap illumination sources. Photoetching the surface can produce μm -sized porous structures which have subsurface chambers produced by undercutting during the etching process. The dye sensitization quantum yield per incident photon at a single wavelength on some n- SnS_2 crystals increases from 0.35% to above 10% after photoelectrochemical etching. A Langmuir analysis of the dye adsorption isotherms reveals that the

enhanced dye sensitization efficiency results mainly from the increased surface area of the photoetched surface.

The sensitized photocurrent for methylene blue shows a different time dependence before and after etching. Depending on the etching condition, the sensitized photocurrent on the surface may decay with time. Quantum yield decreases with increased light intensity were greater on etched surfaces when compared to unetched surfaces. These losses are attributed to the greater mass transport limitations for regeneration of the photooxidized dye molecules by the regenerating agent on etched surfaces relative to that on unetched surfaces.

The results of the studies on the nearly perfect surfaces and on the photoetched surfaces have resulted in both a new model for electron injection into SnS_2 electrodes and in increases in the quantum yield for this electron injection process to well above 10%. We feel that future progress in both the fundamental understanding of the electron injection process and the mechanisms of photoetching will allow us to further increase the quantum yields for electron injection to levels that may be of real interest for solar energy conversion.

The photo-STM proposed in the original proposal has been applied to semiconductor surfaces while illuminated with above bandgap radiation. This experiment was rather easy to perform, since on a good semiconductor material large photocurrent signals could be obtained using lock-in detection. The large signals were useful in developing both the hardware and the understanding of the origins of the signals for eventual extension of the technique to molecular level detection. We are in the process of preparing a publication on the use of this technique on semiconductor surfaces without adsorbed dye molecules. Some of the preliminary results from the technique will be discussed below.

Figure 1 shows an image of a threading dislocation on p-MoS₂. A zigzag pattern is clearly seen in the topography of the sample. The photomap shows

that photo-generated carriers are not collected at the defect (it appears dark in the image) but also the spatial influence of this recombination extends about 100 nm from the actual defect.

Figure 2 shows a natural step on p-MoS₂ and the reduced photocurrent obtained at this step. We are in the process of investigating the photocurrent collection at these edge sites as a function of various surface treatments such as exposure to I₃⁻. Preliminary results show that we can see differences between the photoresponse of treated and untreated surface even though there are no topographic changes after chemical treatment.

Figure Captions

Figure 1 - Image of a threading dislocation on p-MoS₂. The left image is the topography of the sample and the right image is composed only of photo-induced carriers. The right side image clearly shows the carrier loss due to the threading defect. A scale bar indicates the size of the features being imaged.

Figure 2 - Topographical (left) and photo-generated (right) images of p-MoS₂. The step edge traps carriers as do the smaller features seen on the surface of the crystal. Sample bias=900 mV

Photo-generated

Topography

Figure 1

Photoresponse Image

Topographic Image

Figure 2

DOE Supported Publications and Presentations During Period 12/15/92 to 7/15/95

Publications

Xiumei Dou, Laura Sharp, P. A. Morris and B. A. Parkinson, "Increasing the Dye Sensitization Efficiency of SnS_2 Photoanodes by Photoelectrochemical Etching", Langmuir, in press

Xiumei Dou, P. A. Morris and B. A. Parkinson, "Studies of the Sensitization of SnS_2 Photoanodes with a Singlet and Triplet Dyes", Langmuir, in press

D. R. Louder and B. A. Parkinson, "Fundamental Review: Scanning Probe Microscopies", Analytical Chemistry, **66**, 84R-105R, (1994)

D. R. Louder and B. A. Parkinson, "Recent Progress in Scanning Force Microscopies", Analytical Chemistry, **67**, 297A, (1995)

David L. Sampson and B. A. Parkinson, "Tungsten Diselenide as a Substrate for the Imaging of Liquid Crystals by Scanning Tunneling Microscopy", Proceedings of the SPIE, **2384**, 144, (1995)

R. Schlaf, R. Stübner, D. R. Louder, S. Tiefenbacher, H. Jungblut and B. A. Parkinson, "Tip-Sample Interactions in Scanning Tunneling Microscopy: Bias Voltage Dependence of Layer and Edge Heights on Layered Structure Dichalcogenides", J. Vac. Sci. B., submitted

D. R. Louder, R. Schlaf and B. A. Parkinson, "Imaging and Characterization of Dopants in Layered Chalcogenide Semiconductors with Scanning Tunneling Microscopy". J. Applied Phys., submitted

Personnel and Presentations

B. A. Parkinson

STM 95, Snomass, CO, July 1995

2nd International Meeting on New Trends in Photoelectrochemistry, Tokyo, Japan, March 1994

EPSCoR Plenary Lecture, University of South Dakota, July, 1995

ACS National Meeting, Washington, DC, August 1994

University of Wyoming, Department of Chemistry

US-Japan Seminar on Photoelectrochemistry, San Diego, 3/95

Denver University - October, 1993

Local Section of ACS - Fort Collins - Sept. 1993

Materials Research Society, Boston, MA - Nov. 1993

Kodak, Windsor, Colorado - Sept. 1993

Department of Chemistry, University of California, Berkeley, Nov. 1992

Department of Chemistry, University of California, Davis, November 1992

Electron Distributions and Chemical Bonding Gordon Conf., July 1992

American Chemical Society, San Francisco, August 1992

Electrochemical Society, Toronto, October 1992

Laura Sharp - predoctoral student (PhD expected 1997)

36th Rocky Mountain Conference on Analytical Chemistry, Aug 1994

Electrochemical Society, Miami, FL, October, 1994

Rocky Mountain Symposium on Photons and Chemistry, Estes Park, CO,
April 1995

37th Rocky Mountain Conference on Analytical Chemistry, July 1995

Dave Sampson - predoctoral student (PhD expected 1997)

SPIE, Scanning Probe Microscopies III, San Jose, CA, February 1995

American Vacuum Society, Denver, CO, October 1994

STM 95, Snomass, CO, July 1995

Darrell Louder - predoctoral student (PhD expected 1996)

American Vacuum Society, Denver, CO October 1994

STM 95, Snomass, CO, July 1995

Xuimei Dou - Postdoctoral

35th Rocky Mountain Conference on Analytical Chemistry, July 1993