DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FINAL REPORT

of

~~and DE-FC 02-98ER45682~~

"Installation of a Synchrotron Radiation Beamline Facility at the
J. Bennett Johnston, Sr. Center for Advanced Microstructures
and Devices for the Science and Engineering Alliance.
Phase I and II."

for
September 15, 1996
to
December 14, 1999

submitted to the
Office of Energy Research
Department of Energy

by

Robert Gooden, PD and PI
Department of Chemistry
Southern University
Baton Rouge, LA 70813

March 31, 2000

DOE Patent Clearance Granted
MDvorscak
Mark P Dvorscak
(630) 252-2393
E-mail mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office
11-20-03
Date

Final Technical Reports

"EXAFS Analysis of Sulfur K-edge in Rock-Forming Sulfide Minerals",
Innocent J. Aluka, Department of Physics and Earth Sciences,
Prairie View A&M Univ.

Mineral samples of stannite, chalcopyrite, and sphalerite were collected and analysed by EXAFS at SSRL. The data were ratioed as fluorescence/incident flux, IF/I_0 , and the individual sweeps were compared to observe significant differences. The data were processed using the EXAFSPAK programs for X-ray absorption spectroscopy analysis. The sulfur K-edge spectra of the three sulfide minerals showed considerable structure, and could be used as a finger print to identify these minerals. A notable feature in the chalcopyrite spectrum was the prepeak, present in the stannite spectrum to a lesser extent and absent in sphalerite. The sulfur K-edge EXAFS was found experimentally difficult to collect. The data collected would not be suitable for a detailed analysis.

I. "Deep UV Photochromism of Aberchromes 540 and 670 in Solution and Polymer Matrices" II. "Morphological Changes of UV-Exposed Uniaxially Elongated Poly(ethylene -co- carbon monoxide)".

Robert Gooden, Department of Chemistry, Southern Univ.

The photochemistry of Aberchrome 540 and 670 was studied at 254 nm in chloroform and hexane solutions and in PMMA and poly vinyl butyral, PVB, matrices. The objective was to find materials suitable for deep UV lithographic actionometers and alignment aids. Photolysis of the more reactive Aberchrome 540 using a filtered low pressure mercury lamp to obtain monochromatic 254 nm light, resulted in the formation of a photoproduct which was unstable on further exposure to 254 nm radiation. This photoproduct also absorbed stronger than Aberchrome 540. Results with Aberchrome 670 showed a photoproduct which was more stable than 540P and reverted back to the starting photochromic on standing. The utility of these materials will be limited by their absorption properties at the wavelengths to be used. Further studies at wavelengths below 250 nm and using synchrotron radiation at CAMD were planned.

At CAMD the 7A beamline was redesigned to allow insertion of a silicon mirror in order to reflect UV radiation. The UV radiation would be monochromatized further using band pass filters. Initial measurements indicated that photon fluxes only in the 1-10 microwatts per square centimeter were being transmitted through the window instead of the expected 10-100 milliwatts per square centimeters. Further work on resolving this issue was planned.

Poly(ethylene -co- carbon monoxide) degrades on exposure to UV light by two chain scission reactions. If the polymer is oriented by stretching the morphology changes dramatically. The photochemistry is also altered in the earliest stage due to alignment of the molecular chains in the amorphous regions. Additional changes in the crystalline phases due to stretching and exposure to light were also observed. Small angle x-ray scattering using synchrotron radiation as a source, will allow the observation of this process in real time. Preliminary characterizations of elongated samples using conventional X-ray sources and with synchrotron radiation at the Advanced Photon Source's MHATT-CAT beamline (in collaboration with Walter P. Lowe and Shawn Abernathy, Department of Physics and Astronomy, Howard Univ. and MHATT-CAT, Argonne) were made. Additionally, orientation effects, and polarization effects can be probed.

"Accelerated Illumination of a Fluorinated Amorphous Silicon to Determine Photostability", Hylton G. McWhinney, Department of Chemistry, Prairie View A&M Univ.

Amorphous silicon films were deposited on a variety of substrates, single crystal silicon, sapphire, aluminum, and float glass, by plasma deposition of silane/argon mixture. Fluorinated silicon films were fabricated using mixtures of silicon tetrafluoride/silane/argon mixtures. The films were characterized by X-ray diffractometry, photoelectron spectroscopy, and profilometry. Film thicknesses varied between 0.5 to 0.8 microns to 1.5 to 2.5 microns. It was found that oxygen concentration of the films rose dramatically with fluorine content, regardless as to the substrate used.

Depth profiling of films deposited on pure silicon showed a very thin layer, less than 20 Angstroms, of silicon oxide. It appeared that the presence of fluorine promoted the scavenging of oxygen, probably via a silicon oxyfluoride compound. Other studies were conducted using amorphous silicon modified with elemental fluorine to form an electronically inactive buffer layer and absorb mechanical stress at the substrate-deposit interface. Further studies on the electrical properties on these films were planned. Additionally, it was planned to irradiate these films with a synchrotron radiation solar energy simulator at CAMD. The solar simulator was not developed during the period of this award.

"Investigations of Synchrotron Irradiated Surfaces and Interfaces in MOS Structures", Pradeep K. Bhattacharya and Ajit Singh,

Department of Electrical Engineering, Southern Univ.

In an effort to interpret the behavior of synchrotron irradiated surfaces and interfaces, metal oxide semiconductor (MOS) were assumed as ideal. This study was made on commercial optically fabricated devices and on process induced damages and Si/SiO₂ interfacial damage. We have looked into transconductance and threshold voltage of insulated gate metal oxide semiconductor field effect transistors (MOSFETs). Two types of devices, open and closed (donut) type IGFETs and polygated capacitors as passive devices were chosen. Preliminary tests on the capacitors were made employing an HP4280A C-V meter and recorder. The transistors were measured on an HP4145B semiconductor parameter analyzer and a micromanipulator semi-manual probe.

A first focus was to characterize the unimplanted MOS structures. All Mos structures had the same vertical cross section, gate oxide thickness, and polysilicon gate thickness. A low temperature oxide using standard n-MOS processes capped the devices. The undesirable generation of near interface or bulk charge and annealing of the gate insulator of short channel IGFETs was our second focus. The measured extent of damage was the change in the turn on or threshold voltages as a function of absorbed dose. Adsorbed dosages were calculated using ideal Beer-Lambert's law, neglecting scattering. The XRCL beamline 7A at CAMD was used to produce dosages of 6, 8, and 24 MRads uniformly over samples.

Normal unirradiated devices showed a maximum of 10 mV threshold voltage shift. Post irradiation shift was found to increase 6.4%. The process of heat annealing was used to heal the damage due to irradiation. Annealing with a convection microwave source at 450°F in an argon atmosphere for about 20 min repaired the damages. After annealing, the decrease in threshold voltage was reduced to 3%. the same was found for transconductance measurements, except the extent of change, about 34% was larger.

The annealing of implanted devices did not show full recovery and more experiments are needed using both thermal and RF annealing devices. These studies will be continued and extended up to the 100 MRads limit used for defense purposes.

"High Resolution X-ray Imaging", Paul J. Ebert, NOLASCO Science Consultants, Baton Rouge, LA

In the course of this work, over 4,500 exposures were obtained to measure the x-ray optical properties of opaque spheres and micrometer-sized apertures. X-ray shadowgraphs of high quality (Grade 10 or better) spheres of various diameters, materials, and

distances were obtained. In many of these shadowgraphs, an image of the CAMD 1.55 keV x-ray source was obtained. Similarly, with micron-sized pinholes of various diameters and at various distances, x-ray source images were also obtained. A 35 mm camera was adapted to operate remotely in the lithography vacuum chamber.

The camera was loaded with Kodak 2415 film that proved to be sensitive to soft x-rays and have a wide dynamic range and excellent spatial resolution. In separate experiments, the x-ray fluxes were measured with a thin window flow proportional counter to calibrate the film to 1.55 keV photons and a flat bed optical scanner was also set up as a scanning microdensitometer with the aid of a calibrated stepwedge and neutral density filters, a power MacIntosh and image analysis software. Film density was also measured with a MacBeth microdensitometer. Exposures and flux measurements were carried out on the CAMD Beamline VII. No work was done on Beamline V as originally planned.

"Spectroelectrochemical and X-ray Absorption Spectroscopy Investigations of Electrode and electrolyte Materials for Rechargeable Batteries and Fuel Cells", Rambabu Bobba, Department of Physics, Southern Univ.

The primary goal of this project was to investigate electrode-electrolyte interfacial reactions in solid electrolytes for battery and fuel cell applications using spectroelectrochemical and synchrotron radiation EXAFS and XANES techniques. These measurements were made using the double crystal monochromator (DCM) beamline at CAMD. The following systems were investigated; carbon supported noble and transition metal electrocatalysts used in direct oxidation methanol fuel cells (DMFCs), Nafion-type perfluorinated ionomers used as electrolytes in DMFCs, in situ Fe and S K-edge EXAFS spectra of Li/SPE/FeS₂, rare earth dopants in CeO₂ used as solid oxide fuel cells, high lithium ion conducting sol-gel prepared silver selenophosphate, vanadate, and chromate glasses used as electrolytes for high density primary batteries, and EXAFS studies of doped CdTe and ZnTe thin films for solar cells.

X-ray absorption spectroscopy was used to understand the structure of a perfluorinated Nafion. Membranes were analyzed after heat and acid treatment with H₃PO₄. In non-treated Nafion, proton transport is totally dependent on the incorporation of water. Phosphoric acid enhanced the ion conductivity of the membrane.

EXAFS spectra were measured for Pt foil, Pt/Ru/Nafion 115 and Pt/Ru/Nafion 117. There was a striking similarity in data sets for all three. Fourier transforms of the first coordination shell of all three samples were the same. There were significant

differences at the higher coordination shells. Conclusions drawn were the catalyst is not statistical, the metals had an onion geometry with Pt inside and Ru in an outer shell, and there were no significant differences in the geometric structure of the catalyst due to different types of Nafion.

Rare earth doped ceria samples were prepared and measured by XANES. The Ce-L₁₁₁ and rare earth L₁₁₁ edges were measured and compared to data from nontrivalent impurities. Structural parameters for solid solutions were obtained and compared with various defect models.

Low temperature synthesis of Li silicate gels were investigated in order to improve ionic conductivity. Gels were characterized by XRD, XANES, FTIR, SEM, EDS, WDS, and impedance spectroscopy. Samples were found to be highly amorphous. Binary silver silicate-silver oxide-silicon dioxide systems were prepared by sol-gel methods and characterized by XRD, FTIR, WDS, SEM, and impedance spectroscopy. The observed conductivity could be explained using theoretical models.

Participating Students Information

(name, race, gender, classification, major)

Prairie View A&M University

Latisha Griffin, Black female, junior agriculture major.
Darisha McGowan, Black female, junior, science education.
Ronique Williams, Black female, sophomore, science education
Korrie Broomfield, Black female, sophomore, science education.
Nichole Pope, Black female, junior, science education.
Dawn Burton, Black female, undergraduate.
Tony Grady, Black male, graduate.
Keisha Phipps, Black female, undergraduate.
Andrea Ashley, Black female, graduate.

Southern University

Danica Smith, Black female, undergraduate, chemistry.
Hazel Labode, Black female, undergraduate, chemistry.
Hazel Labode, Black female, undergraduate, chemistry.
Latisha Johnson, Black female, undergraduate, chemistry.
Rolanda Johnson, Black female, undergraduate, chemistry.
Veronica Holmes, Black female, undergraduate, chemistry.
Alica Wiltz, Black female, undergraduate, chemistry.
Candice Roberson, Black female, undergraduate, chemistry.
Lisa Davis, Black female, undergraduate, chemistry.
Tamika Taplin, Black female, undergraduate, chemistry.
Marcus Etienne, Black male, undergraduate, chemistry.
Teora Tyrone, Black female, undergraduate, chemistry.
Melvin Smith, Black male, undergraduate, electrical engineering.
Jeremiah Grey, Black male, undergraduate, physics.
Tameka Page, Black female, undergraduate, physics.
Lumamba Bartlow, Black male, undergraduate, chemistry.
Leah Warrington, Black female, undergraduate, chemistry.
Rhonda Johnson, Black female, undergraduate, chemistry.
Don Thomas, Black male, undergraduate, physics.
James Baker, Black male, undergraduate, physics.
Vernita Young, Black female, undergraduate, physics.
Donald Prier, Black male, graduate, physics.
Tommy Rockwood, Black male, graduate, physics.
V. Shanta, Asian/PI, graduate, physics.
Darren Gordon, Black male, undergraduate, electrical engineering.
Elijah Lubandi, Black male, undergraduate, electrical engineering.
Derrick Bell, Black male, undergraduate, electrical engineering.
Randall Anderson, Black male, undergraduate, electr. engineering.
Marvin Carter, Black male, undergraduate, electrical engineering.
Kevin Calvin, Black male, undergraduate, electrical engineering.
Fabian Thomas, Black male, undergraduate, electrical engineering.
Robert Osborne, Black male, undergraduate, electrical engineering.
Lawrence Savage, Black male, undergraduate, electr. engineering.

Angela Davis, Black female, undergraduate, electrical engineering.
Tiffany Moore, Black female, undergraduate, electrical engineering.
Dawn Elsey, Black female, undergraduate, electrical engineering.
Tho Phan, Asian/PI, undergraduate, electrical engineering.
Malini Sriramraja, Asian/PI, undergraduate, electrical engineering.
Luan Pham, Asian/PI, undergraduate, electrical engineering.
Darmesh Shah, Asian/PI, undergraduate, electrical engineering.
Tam Thai, Asian/PI, undergraduate, electrical engineering.