REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) 05-11-2014		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Aug-2013 - 31-Jul-2014	
4. TITLE AND SUBTITLE Final Report: Implementation of Inverse Photoelectron Spectroscopy for Measuring the Empty Electronic States of Metal Oxide Surfaces			5a. CONTRACT NUMBER W911NF-13-1-0320		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611103		
6. AUTHORS James E. Whitten			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Massachusetts - Lowell Office of Research Administration 600 Suffolk Street, Suite 226 Lowell, MA 01854 -3643			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 63442-CH-RIP.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
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15. SUBJECT TERMS photoelectron spectroscopy, inverse photoelectron spectroscopy, metal oxides					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON James Whitten
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 978-934-3666

Report Title

Final Report: Implementation of Inverse Photoelectron Spectroscopy for Measuring the Empty Electronic States of Metal Oxide Surfaces

ABSTRACT

Inverse photoelectron spectroscopy (IPES) has been implemented at the University of Massachusetts Lowell through this ARO-funded DURIP award. The instrumentation consists of a low energy electron gun and a photon detector installed in an ultrahigh vacuum (UHV) chamber. When impinging electrons land in unoccupied electronic states, photons are emitted which contain information regarding the energies of the states. The UHV chamber was already in place at UMass Lowell, and the IPES equipment and associated electronics were added to it. This UHV chamber already had ultraviolet photoelectron spectroscopy (UPS) capability. The combination of UPS and IPES in the same instrument makes possible measurements of the energies and densities of filled and empty electronic states. Testing of the instrument is now complete, and initial results on oxidized zirconium have been performed.

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Scientific Progress

See attachment

Technology Transfer

We have strong interactions with the chemical/biological filtration team at the Edgewood Chemical and Biological Center (ECBC). The IPES instrument implemented with funding from this DURIP will help us understand surface chemistry issues of relevance to their research.

Final Report
DURIP: Implementation of Inverse Photoelectron Spectroscopy
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Lowell, MA 01854

Inverse photoelectron spectroscopy (IPES) measures the energies and densities of unoccupied orbitals and states on surfaces. In this technique, low energy electrons impinge on a sample and land in empty electronic states. In the Bremsstrahlung isochromat spectroscopy (BIS) mode, impinging electrons in an initial state of energy E_{initial} (i.e., the kinetic energy of the electrons) make a transition to an empty, final state of energy E_{final} , where E_f is below the vacuum level. To conserve energy, a photon of energy $E_{\text{initial}} - E_{\text{final}}$ is emitted. The energy difference between the initial and final states results in the emission of a photon. If the energy of the impinging electron beam is varied, and photons in a narrow band of energy are measured, then the energies of the unoccupied electronic states can be measured. The DURIP grant has allowed us to implement this technique at the University of Massachusetts Lowell.

Major components include a low energy electron gun under the control of a computer and a narrow band photon detector. This equipment and associated electronics were purchased from PSP, Inc. Supporting instrumentation, including an ion gun and turbomolecular pump were also purchased from the DURIP funds. This equipment was installed in an existing photoelectron spectrometer in the Whitten group. The spectrometer into which they were installed already had the capability of performing X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). XPS is mainly useful for surface chemistry and elemental analysis measurements, and UPS permits measurement of the energies and densities of the filled electronic states. Therefore, the combination of UPS and IPES allows both the filled and empty electronic states to be measured on metal and semiconducting surfaces.

Figure 1 shows a photograph of the ultrahigh vacuum (UHV) machine that now contains the IPES equipment. The instrument consists of two chambers, with the right one in the photo (the analysis chamber) containing the new equipment. The low energy electron gun and photon detector are aimed at the sample, which is situated in

approximately the center of the right-most chamber. The left chamber contains auxiliary equipment, including a mass spectrometer for thermal desorption and a Kelvin probe.

Figure 1: Photograph of the photoelectron spectrometer at the University of Massachusetts Lowell into which the IPES equipment has been installed. The low energy electron gun is at the very bottom right of the photo and is on a retractable bellows. The photon detector is not easily visible in the photograph.

The equipment was successfully installed, and initial IPES experiments have been performed. Of particular relevance to ARO/DTRA are measurements of the electronic structure of metal hydroxides and oxides and how this is affected by adsorption of hazardous gases. Ultimately, we are interested in correlating adsorbate-induced changes in the electronic states of the surface with changes in the photoluminescence spectrum.

The results of some of our first experiments on zirconium oxide are shown in **Figure 2**. This figure is a combination of UPS and IPES data, using the instrument in **Figure 1**. The black curves are for unexposed or “clean” zirconium oxide. The occupied valence electronic states are mainly composed of oxygen 2p electrons. The unoccupied states are zirconium 4d electrons. It is

somewhat surprising that methanethiol dosing does not change the spectra more, but there is a change in the filled states, as seen by the shift in the O 2p electrons toward the Fermi level.

Figure 2: Combined data from UPS and IPES showing the frontier occupied electronic and near edge unfilled states of oxidized zirconium before and after exposure to 300 L of methanethiol gas. The spectra to the left of zero on the energy scale were measured using UPS, and the spectra to the right of the zero scale were measured with IPES. The IPES curves have been multiplied by 50 for ease of viewing.

The IPES instrument is working well, and more experiments are being performed. These include sputter cleaning zirconium, performing UPS and IPES to measure the band structure, and then leaking in water vapor to adsorb hydroxyl groups. UPS and IPES will then be remeasured. Various gases, including sulfur dioxide, will subsequently be admitted. Our research indicates that SO_3 replaces the hydroxyl groups and markedly changes the photoluminescence spectrum of particulate $\text{Zr}(\text{OH})_4$. It will be important to measure how the IPES and UPS spectra change due to sulfite adsorption. This will increase our knowledge of the mechanisms involved in the observed photoluminescence changes.