"A STUDY OF ELECTRON AND UV PHOTON SURFACE INTERACTIONS"

PROGRESS REPORT

David Lichtman

University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

March 1, 1974 - February 28, 1975

PREPARED FOR THE U.S. ATOMIC ENERGY COMMISSION
UNDER CONTRACT NO. AT(11-1)-2425

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or 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.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

"A Study of Electron and UV Photon Surface Interactions"

Principal Investigator: David Lichtman

PROGRESS REPORT

ABSTRACT

The main electron-induced desorption system has been considerably modified. A new gas-phase RGA has replaced the old one, increasing the sensitivity for neutral detection by about 10^5 . Special electron guns and control units have been designed and constructed to enable experiments on E.I.D. over the energy range 0-20KeV. A special ion gun has been constructed and added to the system to allow for sputter-cleaning of samples and to enable us to perform Secondary Ion Mass-Spectroscopy as well. Some preliminary experiments on electron-induced H^+ and F^+ from stainless steel over the temperature range of -196 C to +300 C show a considerable cross-section ($\approx 10^{-18} \text{ cm}^2$) and a definite correlation between the two desorbing ion signals. In the photodesorption work, measurements are being made on zinc oxide since it is presently believed that photodesorption is related to semiconductor substrates. Photodesorption occurs readily from zinc oxide substrate and specific data has been taken on photodesorbing oxygen (O), carbon dioxide, carbon monoxide, hydrogen, etc. Preliminary results indicate cross-sections for photodesorption of approximately 10^{-17} cm^2 for O and approximately 10^{-19} cm^2 for CO_2 . Measurements on photoconductivity show changes, some of which seem to be related to gas adsorption and desorption.

LEGAL NOTICE

"This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Atomic Energy Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or,
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

As used in the above, 'person acting on behalf of the Commission' includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor."

"A STUDY OF ELECTRON AND UV PHOTON SURFACE INTERACTIONS"

PROGRESS REPORT

INTRODUCTION

Work on this program has developed along two parallel lines, one related to electron-induced desorption and the other related to photodesorption. Although much work has been done in recent years on low energy electron-induced ion desorption, very little information is available on higher electron energy effects and on neutral desorption. Considerable initial effort, therefore, went into modifying the existing equipment to enable us to work on these two very important areas. In regard to photodesorption, major effort has gone into attempts to determine the basic mechanism and toward that end, considerable work has been done with zinc oxide substrates. These latter experiments are related to the possibility that photodesorption occurs only on semiconductor surfaces. Details of both activities are discussed in the following sections.

ELECTRON-INDUCED DESORPTION

Two main activities have been pursued on the E.I.D. system. One is significant modifications to the main experimental system, and the other is a continuation of some interesting studies concerning electron-induced H^+ and F^+ signals. In regard to the first matter, we have designed and built a control unit for an electron gun enabling us to work over the entire energy range of 0-20KeV. The electron gun in the system has been completely rebuilt and is now capable of producing a directed electron beam with electron energies ranging from 0eV to at least 5KeV. (An electron gun capable of handling 5KeV-20KeV electrons will be installed at a later date.) We have added an ion gun to the system which can produce a directed beam of ions using accelerating voltages from 0-2.0KV. The Residual Gas Analyzer originally on

this system has been replaced by a much faster and more sensitive model. We have also added a target manipulator with x,y,z and rotational degrees of freedom. Much of this work has involved extensive redesigning, modifications and rebuilding. Preliminary tests have been made on all additions and modifications to the system, and at this time everything is in good working condition.

The designing and building of an electron gun control unit capable of handling electron energies up to 20KeV proved to have its problems. To do controlled E.I.D. experiments it is necessary to have the target maintained at a fixed potential (+1000V - the accelerating potential of the ions for the E.I.I.D. analyzer) over all electron energy ranges (0KeV-20KeV), therefore the filament of the electron gun must be floated at the appropriate voltage (since the first anode and the target are maintained at +1000V throughout the experiment). Consequently the filament current must be supplied by a source floatable to 20KV. This problem was solved by using a large lead storage battery completely isolated by a plexiglass housing. Everything on the control unit at high voltage was isolated to maintain safety even past 20KV by using plexiglass construction throughout. Special plug-in module type resistor banks were designed in order to get variable voltages to vertical, horizontal, and focus plates of the electron gun.

The electron gun in the system was completely rebuilt to handle electrons with energies up to 5KeV. The tungsten ribbon filament was replaced by a smaller lanthanum hexaboride coated rhenium ribbon filament for better performance. A filament mount was added to the gun to make filament replacement quick and easy if the need arose. Apertures, focusing plates, etc., were replaced or added to get a controllable electron beam with spot size at the target variable from .5mm to 5mm - a large improvement over the previous uncontrollable spot size of about 10mm.

An ion gun capable of producing ions accelerated over the

range 0-2KV was also added to the system. By mounting the ion gun flange connector on a bellows extension, and using extension rods of special design to connect the ion gun to its connecting flange, we have the ability of aiming the ion beam at the target over a wide range of target positions. In a system already equipped to do E.I.D. experiments this gives the added capability of doing sputter cleaning and S.I.M.S. (Secondary Ion Mass Spectroscopy).

We also removed the gas phase mass spectrometer previously on the system and replaced it with an R.G.A. with a much greater sensitivity and shorter response time. This new mass spectrometer addition has an electron multiplier instead of a simple Faraday cup collector, thus increasing the sensitivity by a factor of about 10^5 . An FET input preamplifier is connected to the detector end of this R.G.A., thus giving us a much faster response time by decreasing the original RC time constant of several hundred-milliseconds by many orders of magnitude. This addition to the system should make it possible to obtain useful data on electron-induced neutral desorption - an area where little has been done to date.

The addition of the x,y,z and rotary motion target manipulator to the system gives the advantage of being able to optimize the electrostatic focusing condition for E.I.D. studies by proper positioning of the target, thus increasing the sensitivity of our instrument to its maximum. This will also speed up each experimental run enabling us to study more incremental energy ranges and various different possible fusion wall materials.

At this point we have tested all the equipment quite thoroughly and everything works as well or better than we could expect. The critical positioning of several important components inside the vacuum system has been completed to our satisfaction. We are now ready to reinstall the modified and improved cylindrical shield inside the system, enabling us to continue controlled E.I.D. experiments at the higher electron energies.

Some interesting studies were continued concerning F^+ and

H^+ desorbed from stainless steel by 180eV electrons over the temperature range of $-196^\circ C$ to $+300^\circ C$. Both F^+ and H^+ E.I.I.D. signals were large at $-196^\circ C$ and they continued to show a certain definite correlation with each other as the stainless steel sample was cycled from $-196^\circ C$ to $+300^\circ C$ and back again. This H^+ and F^+ E.I.I.D. signal correspondence may be of some importance when considering fusion reactor wall material, especially in light of other E.I.I.D. work showing evidence of fluorine surface migration from warm to cold regions. Eventually we want to continue this low temperature study of F^+ and H^+ on stainless steel at higher electron energies, but it will first be necessary to equip our manipulator with liquid nitrogen cooling.

PHOTODESORPTION

The vacuum system used to observe photodesorption was especially designed for this purpose. A mass spectrometer, which is located 6cm from the sample, has been modified for the detection of neutral species which are desorbed from the sample. This modification has helped to increase the sensitivity of the instrument, thus yielding a capability of detecting partial pressure changes of 10^{-13} Torr.

The system has an auxiliary port for the purpose of mounting an ion gun. The ion gun we are using was originally built for another vacuum system, and has been altered to increase its ion current output. With this altered gun, it is possible to ion-sputter clean the surface of the sample in a short time.

Earlier results obtained on stainless steel and various pure metals led us to speculate on the possibility that photodesorption occurs only from semiconductor surfaces (such as the chromium oxide surface of stainless steel). To test this approach we decided to study photodesorption from a well-known, U.V. active semiconductor, zinc oxide. With this material we could measure both photodesorption and substrate conductivity changes so that we might elucidate the basic mechanisms involved. As a start we considered the possibility of photodesorption of oxygen from zinc

oxide since this process has been extensively considered by semiconductor scientists.

The study of the photodesorption of oxygen from ZnO required the ability to adsorb oxygen onto the substrate. This was accomplished by adding a tank of research grade oxygen to the gas manifold. The oxygen tank plus gas regulator were connected to the manifold by copper tubing.

To determine the spectra available from the high pressure mercury lamp, with its roundel filter, (to be used for some of the experiments), a McPherson .5 meter scanning monochromator with a grating for the wavelength region 3000Å-6000Å was used. The detector used with the monochromator was a EMI photomultiplier that was sensitive in the same wavelength region. With this arrangement the UV lamp was found to have its major line at 3650Å. The intensity of the radiation at the sample surface was measured to be 20mW/cm^2 .

A special small vacuum system was constructed to allow fast preliminary measurements of the electrical properties of the samples to be studied. The system was designed to achieve an ultimate pressure of 10^{-5} - 10^{-6} Torr. It is pumped by an oil-sealed rotary pump, with a liquid nitrogen trap and has ion and thermocouple gauges for pressure measurements. The electrical studies have indicated that powdered samples of ZnO have a resistivity of about 10^5 ohm-cm. With data from both systems, (the small special system and the main analyzing system), it should be possible to correlate the changes of resistivity with the changes in the partial pressures of the desorbing species from the samples.

The electrical and photodesorption measurements of the powder ZnO samples are dependent on their preparation. The following preparation procedure was used. The ultra pure ZnO powder was mixed with deionized water to form a thin chalky solution. The solution was spread uniformly on an alumina sheet 2x4cm and baked in air to 200°C for 3 hours. These samples were studied under a scanning electron microscope (SEM). From these studies

it was found that the powder samples were very porous and therefore have a very large effective surface area.

Sintered and single crystals of ZnO have also been examined by the SEM. The sintered samples were prepared by compressing the ZnO powder to 6,000 psi, and then sintering in a 1000°C furnace for one hour. The SEM micrographs show that the sintered samples were essentially continuous and non-porous. The resistivities of these samples were found to be of the order 100 ohm-cm.

Single crystal samples of ZnO were first mechanically polished. Then they were etched in 10% HCl for 10 sec. to remove the damaged layers due to polishing. Tin contacts were then applied and the resistivity of one sample was about 10^4 ohm-cm. Two other samples will be examined later.

Our present measurements can be divided into two groups: conductivity measurements and mass-spectrometric photodesorption measurements. (Eventually we aim at correlating the data from both.) The measurements were carried out on sintered and powder samples of ZnO. The samples under study are mounted on a special holder that enables heating of the sample as well as monitoring its temperature. The sample conductivity could be measured by a set of four ohmic contacts evaporated onto it. A special window permits illumination of the sample. We used an intense Hg line source centered around 3650Å. This photon energy is slightly greater than the ZnO band gap energy.

A general pattern of behavior emerged in the conductivity measurements done under high vacuum. A typical example is shown in Fig.1. At the onset of illumination the conductivity rises rapidly from its "dark" value σ_0 . The fast rise of about 10% of σ_0 is followed by a much slower rise over a period of many minutes. This increase is generally believed to be a bulk photoconductivity effect which may be followed by surface oxygen photodesorption due to the hole-electron pairs generated by the light. When the light is turned off, a decay of the conductivity follows, usually at a rate slower than its rise. The conductivity

decays to a value higher than σ_0 , the difference being accounted for by the depletion of oxygen. Subsequent admission of oxygen brings the conductivity down to its former value - σ_0 , as shown in Fig.1.

In order to understand the relation of these phenomena to surface processes, we conducted a series of mass-spectrometric measurements on some powder samples, which have a large effective surface area. The sample was treated with one atmosphere of O_2 at about $100^\circ C$ for about 20 minutes. Then the system was pumped down to about 1×10^{-9} Torr and the sample was illuminated for periods of half a second with a low duty cycle in order to eliminate thermal effects. Simultaneously the mass-spectrometer monitored a selected m/e signal.

During ultraviolet radiation a significant increase in the $m/e = 16, 44$ and sometimes 28 signals was found. An example is shown in a chart recorder display (Fig.2). The solid line is the mass-spectrometer output, while the dotted line is the total pressure detected by a Bayard-Alpert type ionization gauge. The total residual pressure increased by a factor of 2 to 6 and the rise was very fast. The ratio of the changes of the 16 and 44 peaks was about 1:5.

In order to check our assumption that the $m/e = 16$ response was due to atomic oxygen we checked the $m/e = 15$ signal, which showed no response during illumination. This eliminates the possibility of the $m/e = 16$ signal being due to CH_4 desorption. Similarly, no response was detected in the O_2 , H_2 , H_2O and other possibly related peaks. Usually there is also a considerable CO response but it has a different pattern which seems to imply perhaps a thermal origin. Preliminary measurements showed that the photodesorption response is higher at elevated temperature, so most of our experiments were carried out at $100^\circ C$. We plan to work at even higher temperatures with suitable heating elements.

We then measured the O and CO_2 yield as a function of net exposure time. The results show an exponential decay behavior of yield vs. illumination time with time constants of 2 and 85

seconds for O and CO₂ signals respectively. This indicates first of all that the m/e = 16 signal is not just a cracking pattern of the CO₂ and secondly that we have a process that can be formulated by:

$$\frac{dn}{dt} = A_p n \phi$$

Here n = density of adsorbed species on the surface, ϕ = photon flux, and A_p = the cross-section for photodesorption.

Knowing ϕ , we have calculated the cross-sections for O and CO₂ desorption which turn out to be $\approx 10^{-17}$ and $\approx 10^{-19}$ cm² respectively. This may vary somewhat from sample to sample but the order of magnitude is significant.

Measurements of the time dependence of the yield were also carried out as a function of the illumination intensity. The preliminary results displayed in Fig.3 show a linear dependence of the time constant on the photon flux, in agreement with the proposed first order quantum mechanism considered. Fig.3 is also an example of the exponential behavior of the yield vs. exposure time.

From the results to date it seems clear that further experiments correlating the desorption with conductivity changes and with the radiation frequency will enable us to develop a more conclusive model of the photodesorption process.

Relative Conductivity

FIG. 1 : Relative conductivity of a sintered ZnO sample as a function of time. The conductivity rises from its "dark" value at the onset of illumination and decays when the UV light is turned off. It reaches its former value only when oxygen is admitted into the system.

FIG. 2 : Relative changes of $m/e = 16$, and 44 signals (solid line) and total pressure (dashed line) during UV radiation for 10 second intervals.

FIG. 3 : CO₂ signal from the mass spectrometer tuned to $m/e = 44$ as a function of net illumination time for two different light intensities (4×10^{16} photons/sec - full circles and 2×10^{16} photons/sec - full triangles).