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A STUDY OF ELECTRON AND UV PHOTON
SURFACE INTERACTIONS

Progress Report
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"A Study of Electron and UV Photon Surface Interactions"

Principal Investigator: David Lichtman

PROGRESS REPORT.

ABSTRACT

Precise reproducible data has been obtained on electron-induced H^+ and F^+ from room temperature stainless steel for electron energies from 0-6,000 eV. Cross section versus energy curves are quite similar to equivalent electron-gas phase molecule interaction curves. The main difference is that for EID for primary electron energies greater than a few hundred eV, reflected primaries and secondary electrons are the dominant contributors to the desorption process. Data to date indicate maximum cross section values for electron induced ion desorption of about 10^{-18} cm^2 and for neutral desorption, of about 10^{-16} cm^2 .

A major effort utilizing primarily zinc oxide surfaces has led to a much better understanding of the mechanism for photodesorption. On many semiconductor surfaces (including the surfaces of stainless steel) oxygen chemisorbs onto impurity carbon atoms. Band-gap and higher energy radiation produce electron-hole pairs. The holes migrate to the surface recombining with the electrons involved in the chemisorption bond. The weakly bound physisorbed CO_2 is then thermally desorbed. Maximum cross sections for this process are the order of 10^{-17} cm^2 .

ABSTRACT (continued)

A critical review of the literature in both photodesorption and EID has been undertaken. All of the literature material has been accumulated, catalogued and analyzed. The final detailed critical review is in preparation and will be forwarded by February 1976.

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PROGRESS REPORT

INTRODUCTION

The plan of work for this year involved three relatively independent activities. One involved continued studies on Electron Induced Desorption, the second was continued study of the photodesorption process and the third was the development of a critical review on both electron and photon induced desorption, especially as they relate to the CTR program. Each of these activities will be discussed separately and a concluding section will consider the status of the overall project.

ELECTRON-INDUCED DESORPTION

The main effort in this area during this past year has been concerned with detailed measurements on electron-induced ion desorption. We have been able to obtain excellent reproducible data on electron induced H^+ and F^+ from room temperature stainless steel, for electron energies from 0-6,000 eV. Much of the details are described in Ref. 4. We believe the relative cross section values to be quite accurate. In addition, preliminary measurements indicate maximum absolute total cross section values are on the order of 10^{-18} cm^2 . The data on the desorbing

H^+ is of special significance since we can make precise comparisons with experimental and theoretical values for electron induced dissociative ionization processes in gaseous hydrogen. Preliminary comparisons indicate that for primary electron energies greater than about 100 eV desorption is caused primarily by reflected primaries and secondary electrons.

One area of this part of the program that has been somewhat delayed is the study of electron-induced neutral desorption. This delay was caused by an unexpected and rather lengthy hospital stay required of the graduate student working on this part of the program. This student, who has exceptional ability and training in this work, is now recovered and work is continuing. Some qualitative data has been obtained and indicates a cross section for neutral desorption of the order of 10^{-16} cm^2 . Quantitative data in this area will soon start to become available, but is not ready for report at this time.

PHOTODESORPTION

During this last year, a major effort in the investigation of semiconductor surfaces led to a better understanding of the mechanism for photodesorption. The work has been done mainly on $\text{ZnO}^{1,2,3,4,5}$ and some on TiO_2^6 surfaces, investigating the photodesorption signal, its mass spectrum, its photon wavelength, photon intensity and temperature dependence and its relation to the surface conductivity and to the surface impurity composition as measured by Auger analysis.

The essence of our results from single crystal and powder samples is that, contrary to the widely held assumption, it is CO_2 that desorbs from ZnO upon band gap irradiation. This is strictly a quantum process, whereby photogenerated holes neutralize the chemisorbed CO_2^- "ion-molecules" on the surface enabling them to desorb readily. Time dependence measurements of the photo-desorption signal show one-to-one correspondence between the p.d. CO_2 signal and the rise in surface conductivity, establishing the role of CO_2 in the process. A calculation of the cross section for this process yields a value of about 10^{-17} cm^2 for the neutralization of CO_2^- by the holes drifting to the surface.

Auger analysis of virgin and illuminated surfaces and chemisorption measurements suggest that the source of the chemisorbed CO_2^- molecules is carbon contamination on the surface. Oxygen can be chemisorbed on active carbon sites on the surface, constituting the CO_2^- molecules, upon electron capture from the ZnO conduction band. Evidence for the proposed mechanism is found in conductivity, chemisorption, and carbon deposition experiments. The process leading to photodesorption of CO_2 appears to be common to many materials, e.g. ZnO, CdS, TiO_2 , stainless steel, etc.

Progress has also been made in photodesorption measurements on metal surfaces. Nb and Ni surfaces show an extremely low cross section for photodesorption after being properly cleaned.

The main effort this past year was to try to develop a

detailed understanding of the photodesorption process. The material in the papers listed, especially Reference 2, indicate that very significant progress was made toward that goal.

CRITICAL REVIEW

As part of the work for this year's portion of the grant we had proposed to complete a detailed critical review of photodesorption and electron-induced desorption especially as they relate to CTR wall problems. The work was divided into two general areas, photodesorption and electron-induced desorption. In the photodesorption area, the material was further divided into two parts according to whether the substrates were metallic or semiconductors and insulators. This separation was determined when it became clear that the process on metals was entirely different from that on semiconductors and insulators. In the area of EID, we have concentrated on material relating primarily to neutral desorption and to general desorption involving high energy primary electrons, that is, greater than a few hundred eV.

Work on this activity has proceeded according to plan. We have accumulated what we believe is a complete listing of papers relevant to photodesorption. The material has been catalogued, read in detail, discussed and analyzed. The final critical discussion and evaluation is complete for photodesorption from metals and will be complete for photodesorption from semiconductors within the next few weeks. The material for the EID

review is virtually complete and the final written version is planned for about January 1976. Thus we expect to submit the final complete critical review for both areas by February of 1976, exactly in accordance with our proposed schedule. We have found that the work involved in these reviews has been extremely valuable to us in our research work and we believe that they will be of considerable value to all those working in the field.

GENERAL SURVEY

An overview of the general progress to date indicates the following status. During the first year, major effort led to optimization of the experimental systems. Effort this present (second) year has concentrated on developing an understanding of the basic mechanisms involved in photodesorption and EID. With the help of the work on the critical review, very significant progress was made in this direction. In addition, preliminary quantitative values are being obtained. Effort is now strongly geared towards obtaining considerable quantitative data. As can be seen in the proposed activity for the next year, effort will continue on the quantitative aspects of these phenomena and it is suggested that preliminary experiments start involving the use of two different bombarding beams simultaneously. Thus, we have an overall long-range plan for developing useful information in this area and we feel that the results to date indicate good progress in following this plan.

During the time of this contract period and until its con-

clusion (March 1, 1975 - February 28, 1976), the principal investigator will have devoted between 25 to 50% of his time to this project.

REFERENCES

1. "Photodesorption From Powdered Zinc Oxide" Y. Shapira, S. M. Cox and David Lichtman, Surface Science 50 503 (1975).
2. "Chemisorption, Photodesorption and Conductivity Measurements on ZnO Surfaces" Y. Shapira, S. M. Cox and David Lichtman, to appear in Surface Science 54 43 (1976). *Revised*
3. "Anomalous Effect of Atomic Hydrogen Generated by UHV Components on the Surface Properties of ZnO" Y. Shapira and David Lichtman, submitted to J. Vac. Sci. and Technol. *Revised*
4. "Electron and Photon Induced Desorption" M. J. Drinkwine, Y. Shapira and David Lichtman, submitted to Advances in Chemistry series.
5. "Photodesorption of CO₂ from ZnO" Y. Shapira, S. M. Cox and D. Lichtman, submitted² to J. Vac. Sci. and Technol. *Revised*
6. "Photodesorption From TiO₂" S. M. Cox and D. Lichtman, submitted to Surface Science.