

III. PHYSICAL ELECTRONICS AND SURFACE PHYSICS

Academic and Research Staff

Prof. Robert E. Stickney
Dr. Mark J. Cardillo

Graduate Students

Clifton S. Y. Ching

RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

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1. Interaction of Gases with Solids

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Mark J. Cardillo, Robert E. Stickney

Our objective is to characterize experimentally and analytically the interaction of a variety of gases with semiconductor and metal surfaces from a molecular viewpoint in order to understand and, we hope, to predict the elementary chemical and physical processes that they undergo. We make use of the techniques of modulated free-jet molecular beams, quadrupole mass spectrometry, Auger electron spectroscopy, and ion bombardment under ultrahigh vacuum conditions.

Within the last year we completed a major study^{1, 2} of the interaction of hydrogen with copper, and have reported the first direct experimental evidence of the nature of energy barriers to dissociative adsorption. We obtained several physical insights about the gas-surface interaction potential, including the role of single-crystal terraces, edge or step sites, and grain boundaries on the adsorption and desorption processes. We also demonstrated that an equilibrium treatment of the data which includes detailed balancing is applicable to these results.

In a separate study we have shown that the high-temperature reaction of water and tungsten, which produces a variety of products, is also amenable to an equilibrium type of analysis. We plan to publish a simple version³ of this analysis from which we have found reasonable agreement for the rate of production of these products over a 1500° K temperature range.

Of comparable importance to these quantitative results is the demonstration that our experimental and analytical approach to the study of gas-surface chemical interactions allows us to obtain very significant information about a wide variety of systems involving reactions on or with surfaces. We have, therefore, expanded the range of our investigations to include the following series of reactions with semiconductor and refractory surfaces, as well as important catalytic reactions on metals and semiconductor surfaces.

We are investigating the oxidation of semiconductor surfaces, particularly its dependence on the surface structure and the incident energy distribution of the reactant gas. We have prepared a series of Si and Ge surfaces for study and are exposing them to oxygen molecular beams (mixed with He) with variable (monoenergetic) kinetic and internal energy. We monitor the volatile reaction products (SiO) and the unreacted O₂ with a rotatable mass spectrometer and the surface composition (Si, SiO₂) with Auger spectrometry. We shall also attempt to introduce or monitor surface faults such as ledges, grain boundaries or chemically etched pits. In collaboration with H. F. Dylla and J. G. King of the Molecule Microscopy Group we are attempting to correlate

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changes in the adsorption and reaction rates at these sites by the use of finely focused scanning electron beam stimulated desorption. We shall measure the velocity distributions of desorbing products, as well as those of the evaporating semiconductor material itself. We believe the deviations of these distributions from a Maxwellian at the crystal temperature may provide the necessary insights for modeling the interaction of a solid with the mobile atoms or molecules on its surface.

We are also studying the dissociative adsorption of catalytic reaction products on analogous surfaces of platinum and copper. A series of analogous platinum and copper surfaces has been prepared that includes orientations with a fixed density of step sites. We are exposing these surfaces to molecular beams of CO_2 with variable kinetic and internal energy. We are investigating the role of the energy distributions in the incident gas on the dissociative adsorption probability. The results, when coupled with the catalytic CO oxidation reaction on these surfaces, should give a complete picture of an important surface reaction and provide strong tests of models such as the quasi-equilibrium theory of surface reactions. This study will also furnish valuable information on the chemical dynamics of gas surface interactions. Other molecular species to be investigated include CH_4 , NO , H_2S and SO_2 .

We are investigating the transport of high-temperature materials by chemical reaction. We have nearly completed measurements on the rate of attack of tungsten by water and CO_2 , and are now measuring the steady-state sticking probabilities of the reactants vs the incident flux and surface temperature and the angular distributions of emitted products. Our goal, other than the simple prediction of hot material lifetimes because of the presence of contaminant gases, is to supply our equilibrium model of surface reactions with sufficient detail to check whether it is capable of yielding accurate quantitative prediction, as opposed to qualitative explanation of the reaction scheme.⁴

References

1. M. Balooch, M. J. Cardillo, D. R. Miller, and R. E. Stickney (to appear in Surface Sci.).
2. M. J. Cardillo, M. Balooch, and R. E. Stickney (submitted for publication in Surface Sci.).
3. Y. Look and M. J. Cardillo (to be submitted for publication).
4. J. C. Batty and R. E. Stickney, J. Chem. Phys. 51, 4485 (1969).

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