

## IX. PHYSICAL ELECTRONICS AND SURFACE PHYSICS\*

### Academic and Research Staff

Prof. R. E. Stickney  
Dr. M. J. Cardillo  
Dr. H. R. Patil

### Graduate Students

P. C. Abbot  
M. Balooch

R. H. Habert

T. E. Kenney  
R. L. Levin

### RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

The general purpose of our research program is to study problems relating to the atomic, molecular, and electronic processes occurring at gas-solid interfaces. Examples of these processes are: thermionic emission, surface ionization, adsorption, absorption, oxidation, catalysis by metals, electrode processes in electrical discharges, and the scattering of molecular beams from solid surfaces. Such processes are encountered in thermionic energy converters, electron tubes, ion propulsion engines, lamps, high-speed flight, and high-temperature nuclear reactors. At present, we are concentrating on the following problems.

#### 1. Absorption, Diffusion, and Permeation of Hydrogen Isotopes in Metals

The absorption, diffusion, and permeation of hydrogen isotopes in solids frequently lead to technological problems because hydrogen absorption degrades the mechanical, electrical, and magnetic properties of many materials, and hydrogen permeation results in unwanted losses or gains of gas, especially in nuclear systems where tritium, the radioactive isotope of hydrogen, must be contained. As a consequence, there have been numerous studies of the rates of absorption, desorption, and permeation for various hydrogen-metal systems. The results indicate that, although the rate-controlling process generally is the diffusion of H atoms within the bulk of the material, there are many instances in which the rate appears to be influenced by surface processes, such as: (a) adsorption and dissociation (and the reverse processes, recombination and desorption); and (b) penetration of H atoms from the surface into the interstices of the solid (and the reverse process). The objective of this project is to establish a more detailed description of the influence of surface processes on the rates of absorption, desorption, and permeation of hydrogen isotopes in different metals.

We have formulated a simple theoretical model that leads to an approximate expression for the permeation rate in terms of the kinetics of the surface processes and the diffusion process. The model appears to provide a reasonable explanation of existing anomalous data, i. e., data that deviate from the predictions of the classical permeation equation in which diffusion is assumed to be the rate-controlling process. We now plan to extend the analysis to the transient cases of absorption and desorption. In addition, we are constructing an experimental apparatus for determining the absorption, desorption and permeation rates of hydrogen in various metals (e. g., Nb and V) under conditions where surface processes are expected to be influential (for example, at low pressures and temperatures, and with contaminated surfaces).

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## (IX. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

### 2. Desorption of Hydrogen from Metals

This study is motivated by the fact that the desorption of gases from solid surfaces is an essential step in a variety of processes, such as catalysis, metal purification, and permeation. In the many cases where the gas exists predominantly as atoms on the surface but desorbs predominantly as molecules, a vital step in the desorption process is the recombination of adsorbed atoms to form molecules. In an attempt to obtain a more detailed understanding of the kinetics and energetics of recombination and desorption, we have measured the spatial distributions of hydrogen molecules desorbed from Ni, Fe, Pt, Nb, Cu, and stainless steel. The results for all of these metals show that, if the surface is unintentionally contaminated by the common bulk impurities (carbon and sulfur), the spatial distributions are more narrow than the commonly assumed diffuse pattern,  $\cos \theta$ , where  $\theta$  is the angle of inspection measured from the surface normal. That is, the desorbed  $H_2$  is concentrated in the vicinity of the surface normal to a greater degree than in the case of diffuse emission. Except for Cu, however, the spatial distributions broaden and approach the diffuse pattern as the degree of surface contamination is reduced by ion bombardment and monitored by Auger electron spectrometry. Cu appears to be an exceptional case because its spatial distribution is far from diffuse even when the surface contamination is reduced below the limits of detection. We have recently completed a more detailed investigation of Cu by using single crystals with surfaces corresponding to different crystal planes, and the results show that the spatial distribution depends on the crystallographic structure of the surfaces. To aid us in developing a theoretical interpretation of these data, we now plan to use molecular-beam techniques to determine the adsorption probability for  $H_2$  on Cu crystals for varying energy and angle of incidence of the impinging molecules.

### 3. Dynamics of the Collisions of Atoms and Molecules with Solid Surfaces

Over the past eight years we have performed both analytical and experimental studies of the nature of collisions between gas atoms (or molecules) and solid surfaces. We have concentrated primarily on studies of nonreactive collisions of noble gases and of  $N_2$  and CO with tungsten crystals, and the results illustrate the dependence of the collision dynamics (e. g., the energy and momentum transfer) on molecular mass, angle of incidence, interaction potential, temperature, crystallographic structure, and surface impurities. During the past year we have decided to change the direction of this program toward reactive collisions, such as catalytic reactions and gas-solid reactions, and plans have been made to add a mass spectrometer to our molecular-beam apparatus. In the coming year we propose to begin an investigation of several simple catalytic reactions involving hydrogen (e. g., isotope exchange, atomic recombination, molecular dissociation) on metal surfaces whose structures and chemical composition will be characterized by low-energy electron diffraction and Auger electron spectroscopy. These results should be a valuable supplement to those obtained in our studies of hydrogen permeation and desorption.

### 4. Other Studies

We are now considering several other possible studies, including a fundamental study of hydrogen embrittlement of iron and steels, measurements of adsorption isotherms by means of Auger electron spectroscopy, mass spectrometric measurements of high-temperature gas-solid reactions (for example, oxidation), and the implantation of ions in solids.

R. E. Stickney

A. EXPERIMENTAL MEASUREMENTS OF THE SPATIAL DISTRIBUTION OF H<sub>2</sub> DESORBED FROM COPPER SINGLE CRYSTALS

Joint Services Electronics Programs (Contract DAAB07-71-C-0300)

M. Balooch, R. E. Stickney

## 1. Introduction

In a previous experimental investigation of the spatial distribution of H<sub>2</sub> molecules desorbed from single crystal surfaces [Ni (110) and Ni (111)] and polycrystalline surfaces (Ni, Fe, Pt, Cu, Nb, and 304 stainless steel) Bradley et al.<sup>1, 2</sup> observed that the distributions are strongly dependent on surface composition (i. e., surface impurities). The measured spatial distributions could be described approximately by the form  $\cos^d \theta$ , where  $\theta$  is the angle of inspection measured from the surface normal. These results indicated a basic difference between the surfaces of clean Cu and those of clean Ni, Fe, Pt, and Nb. Clean Cu desorbs H<sub>2</sub> nondiffusely ( $d \approx 4$ ), whereas the other metals have nondiffuse distribution for surfaces composed of more than one element (i. e., impure surfaces), but the distributions become diffuse ( $d \approx 1$ ) as the surfaces are cleaned. Because of this difference we have decided to investigate copper in greater detail by using single crystals [Cu (110), Cu (100), and Cu (111)] to determine whether the spatial distribution depends on the crystallographic structure of the surface.

## 2. Apparatus and Procedures

The experimental apparatus is identical to that described previously.<sup>1</sup> The experimental technique involves exposing one side of the Cu membrane to H<sub>2</sub> at approximately atmospheric pressure, while the other side is exposed to vacuum. Hydrogen atoms diffuse through the membrane and recombine on the surface to form molecules that desorb into the evacuated chamber. The spatial distribution of the desorbed molecules is measured by a conventional ionization gauge mounted on a rotatable shaft whose center line is tangential to the membrane surface at its center. The membrane is mounted in a manner that enables us to rotate it to various working stations, including an Auger electron spectrometer for determining the surface composition, a rotatable ionization gauge for measuring the spatial distributions, and an ion bombardment gun for surface cleaning.

## a. Sample Preparation

To avoid the possible effect of crystal defects on the spatial distributions, it is desirable to have smooth surfaces that have a minimum of defects. Conventional methods of cutting and polishing Cu single-crystal samples introduce dislocations to a depth of several millimeters below the cut surface.<sup>3</sup> In principle, the crystal can be

## (IX. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

etched to remove the volume containing the introduced dislocations, but it is very difficult to maintain a smooth surface of the desired orientation during such an etch.

Young and Wilson<sup>3</sup> have shown that dislocations are not introduced into copper crystals that have been acid-sawed and acid-polished. Therefore we have adopted their techniques as refined by Ahfarn et al.<sup>4</sup>

The acid saw used for cutting the samples was built in Gordon McKay Laboratories at Harvard University. The cutting solution was 9 parts concentrated nitric acid to 1 part water, and it was fed onto a reciprocating thread. We cut disks, 1.5 mm thick, from single-crystal rods, 1.27 cm in diameter (MARZ grade, Materials Research Corporation), that had three different orientations of the crystal axis [(100), (110), and (111)]. Each disk was electron beam welded at the end of a polycrystalline copper (Materials Research Corporation, MARZ grade) cylinder, 1.27 cm OD and 0.317 cm ID, which was brazed to a stainless-steel tube. This tube was mounted on a rotatable gas manifold and heated by radiation from a concentric tungsten coil, as reported elsewhere.<sup>1</sup>

A method of chemical and electrochemical polishing was used<sup>4</sup> which allows flat surfaces to be produced without introducing dislocations. Chemical cloth polishing was done in 2 stages. In the first stage, a solution was formed by mixing 90 ml of concentrated hydrochloric acid with 10 ml of polyethylene glycol 400. This mixture was saturated with cupric chloride and gaseous hydrogen chloride. One milliliter of a solution of 100 mg of sodium 2-mercaptobenzimidazole 5-sulfonate in 10 ml of concentrated hydrochloric acid was then added to the resultant solution immediately before use, and the solution was vigorously shaken.

The specimens were polished on a piece of percale cotton sheet tightly stretched over a rectangular glass plate. As suggested by Ahfarn et al.,<sup>4</sup> after cleaning the specimen with concentrated nitric acid the solution was poured on the cloth and spread uniformly over the lap. Then the specimen was moved fairly rapidly backward and forward in gentle contact with the lap, with its axis first rotated 20° clockwise and then 20° counterclockwise with respect to the direction of motion. After each 10 transverse motions the crystal was washed with a 10% solution of phosphoric acid containing 1 part in 2000 by volume of a saturated aqueous solution of chromic acid and having a temperature of ~50°C, then it was washed with distilled water and dried in a jet of dry nitrogen.

The specimens were polished with this solution until there was no visible residual surface roughness. At this point we started the second stage, and used the following solution: 200 ml of glacial acetic acid, 200 ml of concentrated hydrochloric acid, 200 ml of orthophosphoric acid, 60 ml of polyethylene glycol 400, and a solution of 100 mg of sodium 2-mercaptobenzimidazole 5-sulfonate in 10 ml of concentrated hydrochloric acid. The mixture was saturated with gaseous hydrogen chloride. Before use, we added 10 ml of a saturated solution of cupric chloride in hydrochloric acid, saturated

with hydrogen chloride, to 50 ml of the solution. Polishing was done on a new lap and, as in the first stage, after 10 polishing motions the crystals were washed with warm 10% phosphoric acid containing 1 part in 2000 by volume of chromic acid solution. This procedure resulted in very smooth surfaces for all three crystal orientations.

Final polishing was accomplished electrochemically. We used Model 451 crystal facing instrument (South Bay Technology, Inc.) with the following polishing solution: 250 ml of 60% orthophosphoric acid, 10 gr of copper carbonate, and 1 ml of chromic acid, saturated solution in water.

#### b. Surface Cleaning

The predominant impurities on the copper single-crystal surfaces were S and C. We found that the most successful procedure for removing these impurities was to bombard the membrane surface with argon ions<sup>5</sup> while maintaining the crystals at the elevated temperature required for measurement of the spatial distribution ( $T \sim 1100^\circ\text{K}$ ). The argon pressure was  $\sim 5 \times 10^{-5}$  Torr, and the ion-bombardment gun was adjusted to provide  $\sim 15 \mu\text{A}/\text{cm}^2$  of 250 eV argon ions to the membrane.

After several hours of ion bombardment, the crystal was heated ( $T \sim 1100^\circ\text{K}$ ) in  $10^{-6}$  Torr of oxygen while a tungsten ribbon at  $\sim 2400^\circ\text{K}$  was placed directly in front of the membrane. The hot tungsten ribbon partially dissociated the  $\text{O}_2$ , thereby providing the atomic oxygen that was required to remove the carbon from the Cu surfaces.

This procedure was repeated several times until C and S were reduced below the limit of detection. Figure IX-1 shows the Auger spectrum of a copper (110) sample after cleaning.

### 3. Results

The spatial distributions of  $\text{H}_2$  desorbed from the cleaned copper single crystals are shown in Fig. IX-2. Since the distributions were almost perfectly symmetric, we have omitted the data for negative values of  $\theta$ . Although the distributions for all three crystal surfaces broadened as the degree of surface contamination was reduced, none became a diffuse distribution in the limit of a completely clean surface. The limiting distribution appeared to be approximately characterized by  $d \approx 2.7$  for Cu (110),  $d \approx 4.8$  for Cu (100), and  $d \approx 6$  for Cu (111). In the case of Cu (110), the distributions were measured for 3 azimuthal orientations ( $\phi = 0^\circ, 45^\circ, \text{ and } 90^\circ$ , as defined in Fig. IX-3). We measured the distributions for Cu (100) at  $\phi = 0^\circ$  and  $45^\circ$  and for Cu (111) at  $\phi = 0^\circ$  and  $90^\circ$ . The data are shown in Fig. IX-4, and we note that the differences among the spatial distributions for varying  $\phi$  are sufficiently small that they are within the limits of our experimental uncertainty. We conclude that the influence of the azimuthal angle on the spatial distribution is quite weak, at best, and perhaps nonexistent.

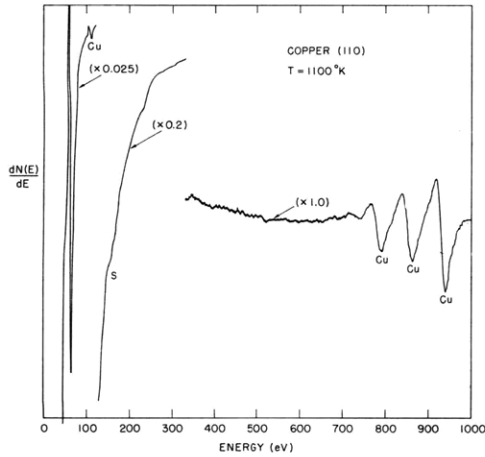


Fig. IX-1.  
Auger spectrum for a nearly clean Cu (110) surface at 1100°K.

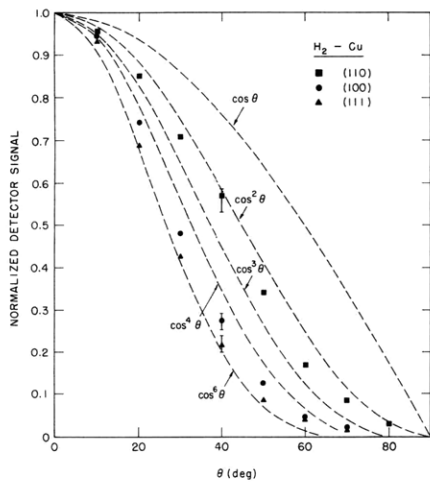


Fig. IX-2.  
Spatial distributions of H<sub>2</sub> derived from nearly clean Cu (110), Cu (100), and Cu (111) surfaces.

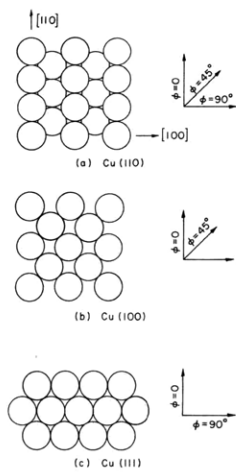


Fig. IX-3.  
Atomic models and azimuthal orientation measurements for Cu (110), Cu (100), and Cu (111).

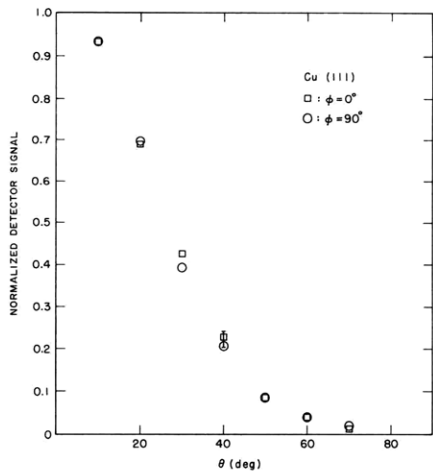
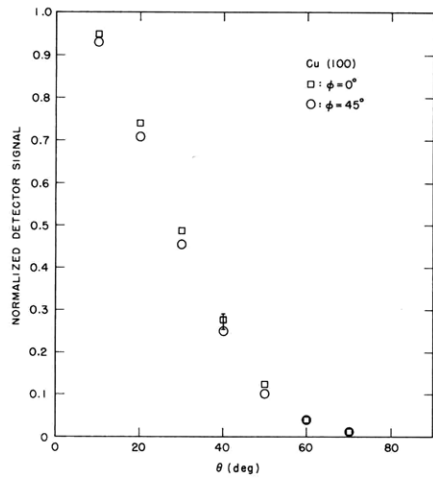
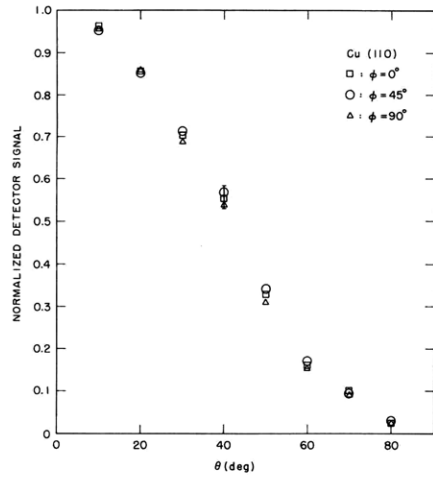


Fig. IX-4. Differences in spatial distributions of  $\phi$  on Cu (110), Cu (100), and Cu (111) surfaces.

## 4. Concluding Remarks

The present results demonstrate that the spatial distribution of hydrogen desorbed from copper depends significantly on the crystallographic structure of the exposed surfaces but does not vary significantly with the azimuthal orientation of the crystal surfaces. It is likely the differences among the crystal surfaces result from the fact that the interaction potential of the H-Cu system depends on the crystal structure of the surface. In the model suggested by Van Willigen,<sup>6</sup> the spatial and speed distributions depend critically upon the height of an energy barrier that is assumed to separate the molecular and atomic adsorption states. In Goodman's model,<sup>7</sup> the distributions depend strongly on the difference between the heat of chemisorption and the heat of dissociation. We have attempted to improve these models by adding the possible influence of the periodic variation of the interaction energy over the surface, but since we have not yet been able to establish a convincing model, we shall postpone our considerations of theoretical models until we obtain additional experimental data. We are now preparing to use molecular-beam techniques to study the probability of adsorption of H<sub>2</sub> on the same Cu crystal planes. By varying the energy and angle of incidence of the impinging molecules and observing the resulting change in the adsorption probability, we hope to obtain new information on the nature of the H-Cu interaction potential.

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