PROGRESS REPORT
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INTERACTIONS ON METALLIC SURFACES

by

Department of Chemistry
and
James Franck Institute
The University of Chicago
Chicago, Illinois 60637

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Prepared by:
Robert Gomer
Professor of Chemistry

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1. Adsorption Studies in the Field Ion Microscope with Argon Imaging
(R. Lewis and R. Gomer)

A question of considerable interest in chemisorption is whether and under what conditions adsorption causes rearrangement of the substrate, i.e., whether it is reconstructive. Low energy electron diffraction (Leed) and conventional field ion microscopy can give only incomplete answers to these questions. The interpretation of Leed patterns is still very ambiguous,\(^1\),\(^2\) and it is now known that in the presence of He at the field of 4.5 volt/Å required for He imaging adsorbates are field desorbed,\(^3\) so that some of the disorder observed may be due not to adsorption but to the desorption act itself. For this reason the use of imaging gases with lower ionization potentials in the field ion microscope is clearly desirable. This has become practical only recently, however, with the advent of the channel plate internal image intensifier,\(^4\) which converts ions into electrons with high gain and no loss of resolution, and circumvents the catastrophic decrease in direct ion energy-to photon conversion efficiency with increasing ion mass. The use of Ar ion microscopy makes it possible to work under conditions where most adsorbates are not field desorbed, and thus throws light on the related question whether adsorbates are visible in the field ion microscope.

Results of experiments carried out with O\(_2\), CO, H, and CH\(_4\) indicate that CO, H, and probably O are not visible in Ar imaging, while CH\(_4\) may be under some conditions. CO adsorption at 78\(^0\)K and 300\(^0\)K does not seem to cause surface reconstruction, but in the presence of Ar, field induced corrosion sets in at \(\mathrm{F}>2.0\) volt/Å and becomes
rapid at 3 volt/Å. Oxygen at 78°K and small coverages seems to cause little reconstruction if any, but the visibility of substrate atoms becomes modified. For coverages close to a monolayer the image contrast vanishes almost totally so that it is difficult to draw unequivocal conclusions. There is some evidence that W-O complexes form and stick out above the surface but this seems to be the exception rather than the rule. Field desorption in the presence of Ar sets in at 2.6 volt/Å and leads to desorption of W as well as O atoms; surface disorder is noticeable after such desorption. H₂ does not seem to affect the surface in any noticeable way, while CH₄ adsorption seems to cause no reconstruction, although field corrosion is rapid above 3 volts/Å. In all cases the (110) plane exhibits very great stability; it is apparently unreconstructed in adsorption and only slightly affected by field-corrosion.

These results indicate that for some systems at least chemisorption per se does not cause reconstruction and that much of the evidence for it previously adduced from He field ion microscopy is the result of disorder caused by field desorption of adsorbate-substrate clusters. At the same time the present results show that the prospects of direct imaging of adsorbate entities are not very good for most electronegative adsorbates.

This work has been written up and accepted for publication.5

2. Mass Spectrometric Desorption Studies
(J. Lopez-Sancho and R. Gomer)

The work carried out during the present contract period has centered on a study of electron impact desorption (EID)⁶, 7, of CO from the (110) plane of tungsten. Previous thermal⁸ and field
emission$^9$ studies have shown that CO on this plane can exist in the low temperature virgin state, which converts on heating to a beta-state; the desorption spectrum of the latter shows a small peak at >900°K, labelled beta-1, and a major one at 1100°K labelled beta-2. In addition readsorption on a beta-layer is known to give electropositive alpha-states.$^9$ Since thermal desorption can give information only on desorbing species, and since work function changes on heating are relatively small and difficult to interpret unequivocally, phenomena below desorption temperatures are difficult to detect by "conventional" methods. Since different ad-species, even of the same substance have different cross sections and may yield different desorption products in electron impact, EID offers a powerful method for investigating processes in adlayers even below desorption temperatures.

Results to date indicate that the principal ionic species are CO$^+$ ($\sigma=5\times10^{-18}$ cm$^2$) for virgin CO; O$^+$ ($\sigma=5\times10^{-18}$ cm$^2$) for beta-1; and CO$^+$ ($\sigma=2\times10^{-17}$ cm$^2$) for alpha. All three states yield some neutral CO. It could also be shown that the conversion of virgin CO to beta-1 occurs from 150°K to 400°K. Further it turns out that beta-1 converts, without desorption, to beta-2 from 400°K to 600°K. It is planned to write up this phase of the work for publication soon.

3. Energy Distributions of Field Emitted Electrons
(P. Young and R. Gomer)

Energy distributions of field emitted electrons are modified by the presence of chemisorbed atoms or molecules and can reveal the location and shape of virtual levels in surface bonding. Retardation analyzers are able to probe the distributions only to within 0.5-0.8 eV of the Fermi level, because of the fact that most of the
emission occurs within that energy range. To probe deeper an energy selector is required. An apparatus incorporating a cylindrical energy analyzer\(^\text{10}\) has been designed and is in the process of construction; this should allow us to probe to at least 3 eV below the Fermi level. The apparatus is intended for use in a cryostat, but is so designed that it can also be used with a conventional ultra-high vacuum system.

References

Publications of Work Resulting from this Contract

Status of Personnel Associated with this Contract
Mr. Richard Lewis received his Ph.D. degree in September, 1970 and has joined the Union Carbide Research Center at Parma, Ohio.

Mr. Jose Lopez-Sancho has returned to his permanent position at the National Research Council in Madrid, Spain.
Dr. Peter Young, who recently received his Ph.D. at Stanford under the guidance of Professor Bienenstock has joined the effort as research associate in October, 1970.

Robert Gomer, principal investigator, returned from his sabbatical leave at the University of Paris, Orsay, France, where he had studied with Professor Friedel, in June, 1970. Since his return it is estimated that he is devoting approximately 65% of his research effort to this program.