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Optical Spectroscopy and Scanning Tunneling Microscopy Studies of Molecular
Adsorbates and Anisotropic Ultrathin Films

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FINAL REPORT

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ABSTRACT

The bonding, chemistry and ordering of molecular adsorbates on well defined single crystal surfaces and in ultrathin films was be studied in an effort to develop sufficient fundamental understanding to allow the controlled preparation of anisotropic ultrathin films of organic monolayers. In this research we combine the use of optical probes (Raman spectroscopy, laser induced thermal desorption with Fourier transform mass spectrometry detection) with scanning tunneling microscopy (STM) and conventional methods of UHV surface science (Auger electron spectroscopy, x-ray photoelectron spectroscopy, low energy electron diffraction, and thermal desorption spectroscopy). The conventional surface probes provide well tested methods for the preparation and characterization of single crystal substrates. The optical probes used in our experiments provide powerful methods for the **molecular identification** of adsorbates in monolayers and ultrathin films. Scanning tunneling microscopy provides us with the ability to determine the detailed molecular level ordering of the molecular adsorbates. The emphasis of this research is on more complex molecular adsorbates some of which are monomer precursors to ultrathin polymer films.

Enhanced methods of Raman spectroscopy have been developed for the study of monolayer adsorbates on surfaces in ultrahigh vacuum environments.

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B. Publications from research supported by DE-FG03-85ER45196

- Reprints
1. Raman Scattering and ATR Studies of Surface-Plasmon Polaritons.
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Physical Review B, **33**, 789 (1986).
 2. Relative Raman Scattering Cross Sections for Chemisorbed and Physisorbed
Pyridine Molecules Adsorbed on SERS Active Ag Films in UHV: Local Field Effects
in the Low Coverage Regime.
J. Giergiel, S. Ushioda, and J.C. Hemminger
Physical Review B, **33**(8), 5657 (1986).
 3. Surface Plasmon Polariton Mode Conversion on Rough Surfaces.
J. Giergiel, C.E. Reed, J.C. Hemminger, and S. Ushioda
Physical Review B, **36**(6), 3052 (1987).
 4. Dipole Radiation in a Multilayer Geometry.
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Physical Review B, **36**(9), 4990 (1987).
 5. Surface Plasmon Polariton Enhancement of Raman Scattering in a Kretschmann
Geometry.
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 6. Growth and Chemistry of TCNQ films on Nickel(111),
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Surface Science, **255**, 31 (1991).
 7. Beam Induced Modifications of TCNQ Multilayers,
S.K. Wells, J. Giergiel, T.A. Land, J.M. Lindquist, and J.C. Hemminger
Surface Science, **257**, 129 (1991).
 8. Direct Observation of Surface Reactions by Scanning Tunneling Microscopy:
Ethylene $\rightarrow$ Ethylidyne $\rightarrow$ Carbon Particles $\rightarrow$ Graphite on Pt(111)
T.A. Land, T. Michely, R.J. Behm, J.C. Hemminger, and G. Comsa
Journal of Chemical Physics, **97**, 6774 (1992).

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C. Overview of Recent Research Results

1. Construction of UHV Variable Temperature STM

In collaboration with the research group of Professor George Comsa, IGV/KFA, Jülich, Germany, we have demonstrated that the ability to vary the sample temperature in conjunction with UHV STM experiments can result in substantial new insight into reaction chemistry on metal surfaces¹⁰⁻¹². In particular, in that work the variable temperature UHV STM allowed us to discover that the partial dehydrogenation of ethylene on Pt(111) to form ethylidyne proceeds most rapidly at boundaries between islands of unreacted ethylene and the product ethylidyne. A major aspect of the work under this project during the last two years has been the construction in my laboratory at UCI of a UHV STM with variable temperature capability based on the technology developed in Professor Comsa's laboratory. The instrument which we have constructed has been designed specifically with surface **chemistry** studies in mind.

Important characteristics of the new instrument are:

- a. Connection between Controlled Atmosphere Glove Box and the UHV chamber.
- b. Two highly stable "Beetle type" STMs^{13,14} -one in the glove box under controlled atmosphere and the other in the UHV chamber.
- c. Variable sample temperature capability with immediate high resolution sample imaging for the UHV STM in the temperature range of ~120K to >500K.
- d. Conventional surface analysis/preparation methods of: Auger electron spectroscopy (AES), Low energy electron diffraction (LEED), quadrupole mass spectrometry, differentially pumped ion gun, and gas dosing capabilities.
- e. Specially designed manipulator which allows the transfer of the sample to and from the STM and surface preparation/analysis techniques **at temperature** (120K to 500K).

Figure 1 shows a schematic drawing of the complete instrument. Including the UHV-STM chamber, the controlled atmosphere glove boxes and the sample transfer chamber connecting the two environments. Figure 2 shows an atomic resolution image of a Au(111) facet on an annealed evaporated gold film, which was obtained with the STM in the controlled atmosphere glove box. A UHV sample manipulator allows, at temperature, transfer of the sample to and from the STM and the other UHV surface experiments (AES, LEED, ion bombardment, gas dosing, etc.). We have just begun taking data with the UHV STM. Our initial studies are involved with ordering of aromatic hydrocarbons and investigation of the carbon particles formed in the dehydrogenation of hydrocarbons on flat Pt(111) and sputtered Pt(111). These experiments are discussed in more detail in the later section which describes our research plans.

FIGURE 1A. Schematic of the combined STM facility. The facility contains two beetle type STMs. One is housed in the dedicated Single Glove Box. The other is housed in the UHV chamber and has variable sample temperature capability.

Figure 1B. Schematic of the UHV chamber part of the instrument. The UHV-STM is housed in the lower part of the main UHV chamber. The sample manipulator allows movement of the sample from the upper level chamber which houses, Auger electron spectroscopy, LEED, ion bombardment and mass spectrometry capabilities to the lower chamber where the sample is transferred (at temperature (120K to >500K) to the STM.

Figure 2a 5000Å X 5000Å image of an annealed gold film. The reconstruction pattern of the (111) facets is clearly visible.

Figure 2b High resolution image of gold film (75Å X 75Å).

2. Analysis of STM images

As will be described in more detail below, we are interested in the ordering of hydrocarbon adsorbates in monolayers on single crystal metal surfaces, and the effect of coadsorbates and substrate defects on that ordering. Variable temperature UHV STM provides an exceedingly powerful tool to study the details of such ordering phenomena. It is important however, to go beyond the stage of just looking at an STM image and saying ordering exists or the monolayer is "highly ordered" or "partially ordered." As such, we have expended some effort to develop ways to quantify molecular ordering as observed in STM images. Initially, we are most interested in aromatic hydrocarbon adsorbates such as that shown in figure 3 which shows a partially ordered monolayer of naphthalene on Pt(111) after annealing the sample to 400K. Two kinds of ordering are easily distinguished in this image: orientational ordering of individual molecules relative to each other and the substrate, and a packing ordering which determines the intermolecular spacing. A simple method to quantify ordering in such a system is to simply generate the molecule center radial distribution function to indicate the "packing" order and an orientational angular radial distribution function¹⁵ to indicate the degree of orientational order. To generate these distribution functions, one needs the coordinates of the center of each molecule and the orientation angle for each molecule. These coordinates and angles can be generated manually using standard image processing software. In this manner we have developed simple computer programs which generate the appropriate distribution functions from individual images. The process of manually identifying the center and orientation of each molecule in an image is sufficiently tedious that the accumulation of statistically significant amounts of data is not routine. At the present we are working on the computer automation of the generation of the list of molecular center coordinates and orientation angles.

Figure 3. STM image of naphthalene adsorbed on Pt(111) after annealing which leads to partial ordering.

In essence this requires application of modern image recognition algorithms to our data, which is under development at present. Application of such techniques should allow us to compare ordering of statistically significant numbers of molecules in statistically significant numbers of images.

In addition to the construction of the STM instrumentation described above, we have continued our activities in two major areas: the growth of rare earth-transition metal intermetallic single crystalline thin films, and electron beam induced chemistry of monolayer and multilayer adsorbates. Our recent results in these areas are described below.

3. Growth and Chemistry of Intermetallic Single Crystal Ultrathin Films

There is significant interest in both the electronic structure¹⁶ and the surface chemistry^{17,18} of intermetallic compounds of the rare earth elements with transition metals. From the electronic structure standpoint several of these systems exhibit heavy Fermion and valence fluctuation behavior. In addition several such systems have been proposed as precursors for rare earth containing catalysts and as such the surface chemistry is of interest.^{17,18} We have focused our efforts on intermetallic compounds of cerium with transition metals. Most of the work carried out previously has involved polycrystalline samples or small single crystals which were prepared by high temperature techniques and contain substantial surface impurities. We have taken the approach of growing thin films of cerium by ultra high vacuum evaporation onto a very clean and well characterized transition metal substrate, followed by annealing under ultra high vacuum. For a number of transition metal substrates, we have found that during the annealing process interdiffusion occurs and a thin film of the intermetallic can be formed. We have used XPS to study this process for a number of polycrystalline transition metal substrates. Thus we have been able to study the valence behavior of polycrystalline intermetallics of cerium with rhenium, iridium and platinum. This work is described in detail in references 19 and 20. In the case of a platinum substrate, we have also carried out the intermetallic growth using a Pt single crystal with (111) surface orientation²¹. In this case epitaxial growth of a single crystalline ultrathin film of the CePt₂ intermetallic is observed. We have studied this epitaxial growth process by low energy electron diffraction as well as XPS. Well defined LEED patterns are obtained consistent with growth of CePt₂ single crystal films. Angle resolved photoemission studies have recently been carried out on this system in collaboration with Andrews, Joyce, Arko, and Thompson of Los Alamos National Laboratory²². The ability to grow very clean, well characterized, single crystalline films of cerium-transition metal intermetallics will significantly enhance the ability of workers in this field to study the details of surface phenomena and electronic structure, without complications due to impurities and unknown surface stoichiometry.

4. Electron beam induced chemistry of TCNQ

Bulk charge transfer compounds of the tetracyanoquinodimethane(TCNQ) have been studied for a number of years as a result of the high electrical conductivity which many such compounds exhibit. We have studied the chemistry of thin films of TCNQ on transition metal substrates to investigate the possibility that polymeric films with moderately high conductivity could be formed. During this period of the grant the adsorption and temperature stability of unmodified and electron-beam modified ultrathin films of the strong electron acceptor, TCNQ, have been studied on a Pt(111) surface by thermal desorption and x-ray photoelectron spectroscopies. At room temperature, a stable multilayer is formed. We find that the first layer of TCNQ forms a negatively charged anion, TCNQ⁻¹, with subsequent layers existing as neutral, molecular TCNQ. Dehydrogenation of the adsorbed species occurs through the loss of HCN and begins at 470K for submonolayer quantities of TCNQ. The primary decomposition products are hydrogen (H₂), hydrogen

cyanide (HCN), and cyanogen (C_2N_2). The changes induced by electron beam exposure include stabilization against thermal decomposition as indicated by TDS and binding energy shifts in the XPS carbon and nitrogen peak positions. In particular, the beam modified material is stable up to approximately 600K at which point the decomposition is observed with evolution of HCN, H_2 , and, at higher temperatures, C_2N_2 . The integrity of the modified material below the decomposition temperature is verified by temperature dependent XPS measurements. As the multilayer is exposed to the electron beam, the characteristic TCNQ spectrum in both the C1S and N1S regions broadens and loses resolution of the shake-up satellite. Upon annealing of the modified film the C1S region narrows further with loss on the high binding energy side and shifts to slightly lower binding energy. Overall, very little of the C1S intensity is lost even upon annealing to 1273K. In the N1S region with annealing significant intensity is lost around 399.5 eV whereupon two peaks are resolved and remain visible even up to 1073K. Upon annealing to 1273K all of the N1S intensity is lost leaving a thick carbon film on the Pt(111) substrate. These changes appear to be consistent with electron beam induced polymerization of the TCNQ.

The high temperature film which is formed from electron bombardment of TCNQ on Pt(111) is a candidate for our STM studies of films formed from the decomposition of hydrocarbons on Pt(111) which are described in the proposed research section of this proposal.

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