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"Structure and Reactivity of Model Thin Film Catalysts"

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Contents

1. Abstract

The purpose of this project is to characterize the structure and reactivity of model bimetallic catalysts, e.g., ultrathin films of Pt deposited on single crystal surfaces of tungsten. Studies during this reporting period (January 15, 1989 to the present) have involved a comparison between the atomically smooth W(110) surface and the atomically rough W(111) surface using several ultrahigh vacuum surface science methods (low energy electron diffraction, LEED, Auger electron spectroscopy, AES, and thermal desorption spectroscopy, TDS). In addition, we have used scanning tunneling microscopy (STM) to provide a microscopic view of Pt induced surface structures with Angstrom level resolution.

On W(110), a single Pt monolayer is stable upon heating to >1800K. It grows in a layer-by-layer mode at 300K, but Pt coverages in excess of one monolayer will cluster into 3-dimensional bulk Pt crystallites upon annealing to $\gtrsim$ 800K.

When W(111) is covered by $\gtrsim 1 \times 10^{15}$ Pt atoms/cm^2 and heated in the range 800-1600 K, the surface undergoes a massive restructuring to form microscopic facets. At 1200 K, the average facet dimensions are ~100Å, and the dominant facet orientation is W(211). The faceting appears to be driven by a Pt-enhanced anisotropy in the surface free energy. To the best of our knowledge, the only other reports of faceting induced by a single monolayer of metal on a metal surface are based on field emission microscopy.

The PI joined Rutgers in Fall 1988, and initiated this project shortly afterwards. It is an outgrowth of work performed by the PI and his colleagues at the National Institute of Standards and Technology (formerly NBS).

2. Summary of Results

a. Introduction

The overall objective of this project is to provide a molecular understanding of heterogeneous catalytic chemistry on well-characterized single crystal surfaces, in particular, to study the relations between surface structure and reactivity over model ultrathin film metal catalysts. Among the areas studied in the recent past are the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen on metal surfaces, the mechanism of catalytic poisoning and promotion, and the reforming of alkanes over model supported Pt catalysts [1-8]. The apparatus employed for these studies contains high pressure reactors contiguous to ultrahigh vacuum surface analysis chambers.

During the last year, we have continued a <u>new effort</u> to study the properties of model thin-film catalysts prepared by evaporating monolayer films of a metal (Pt) onto single-crystal metal substrates (the close-packed W(110) surface and the atomically rough W(111) surface). Such catalysts

serve as model systems for understanding the properties of mixed metal catalysts: these materials have received considerable attention recently because they often exhibit superiority over single-metal substrates as practical catalysts. It is also known that mixed-metal systems can exhibit remarkably different chemisorption properties from those of either metal alone, and we have found striking evidence for this in our own work.

We are studying the growth, thermal stability and surface chemistry of Pt overlayers (sub-monolayer to multiple layer coverages) on W(110) and W(111) by means of a variety of surface science methods, including Auger Electron Spectroscopy (AES), low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS) of a probe molecule, CO, and scanning tunneling microscopy (STM) with Angstrom-level resolution.

b. Pt on W(110)

Based on our studies of Pt/W(110), we find evidence for a strong interaction between platinum and tungsten that causes platinum deposited on tungsten to bind more strongly to the substrate than to neighboring platinum atoms. As a result, heating multiple layers of platinum on W(110) causes all but the first layer to agglomerate into three-dimensional clusters on the surface of the tungsten. The first layer remains dispersed in a single atomic layer with the crystal structure of the underlying tungsten (pseudomorphic structure) and requires a higher temperature for evaporation than does the excess platinum [5].

Until recently, all of the evidence for clustering of Pt multilayers on W(110) was indirect, based on inferences drawn from studies using LEED, Auger electron spectroscopy, ultraviolet photoemission spectroscopy, and thermal desorption spectroscopy (TDS) [5-8]. We are now applying the scanning tunneling microscope to this problem and find <u>direct evidence</u> for the formation of Pt clusters. In one such experiment, a W(110) surface was dosed under uhv conditions with 10 ML of Pt at 300 K, and then heated to 1600 K for one minute. This procedure is believed to cause Pt clusters to form on top of a single Pt monolayer on W(110). The sample was removed from the vacuum system and transported to the laboratory of Professor E. Garfunkel where it was examined using an STM, The Nanoscope-II.

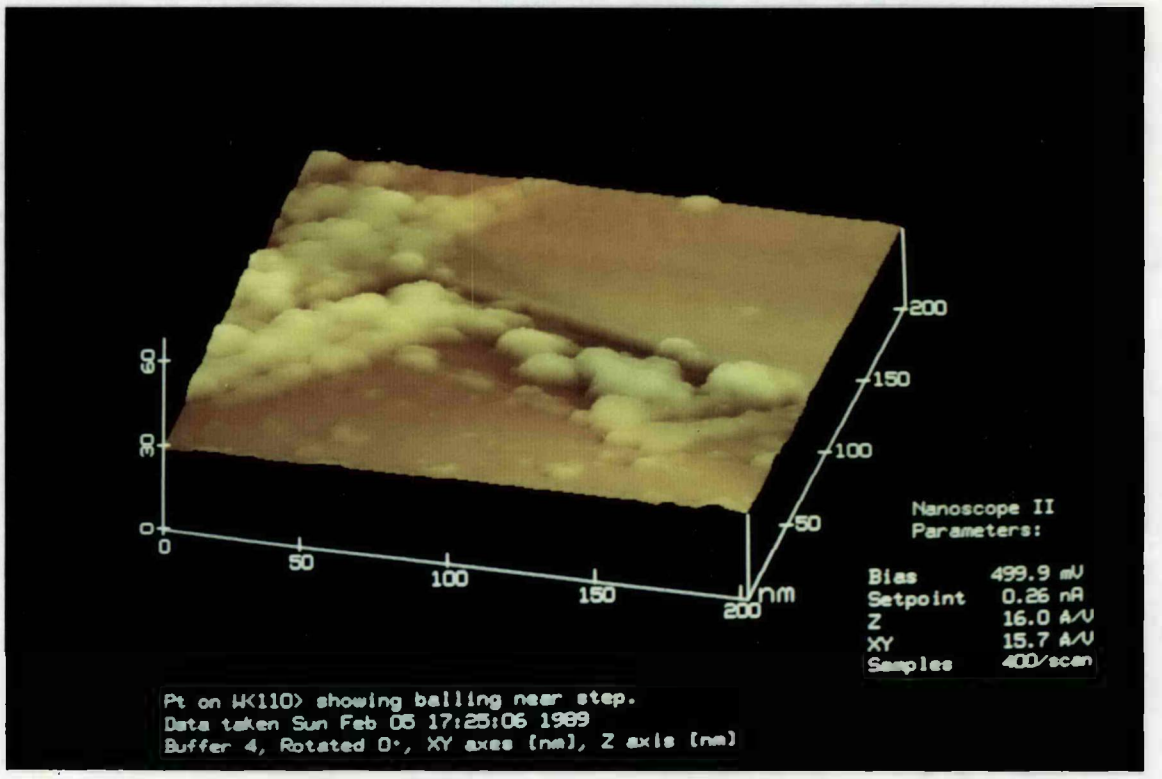

Figure 1
Scanning Tunneling Micrograph of Pt clusters on a W(110) substrate. The surface was prepared by dosing clean W(110) with 10 ML of Pt and annealing at 1600 K in uhv to cause formation of Pt clusters.

Figure 1 shows an STM image of the Pt-covered W(110) surface, and evidence for clusters preferentially decorating atomic steps on the (110) surface is clearly seen. We have observed many such images in which there are large, planar regions (the stable Pt monolayer on W(110)) and other regions where clusters predominate, frequently along surface steps.

c. Pt on W(111)

The behavior of Pt on W(111) is very different from that on W(110): The Pt-covered W(111) surface is unstable upon heating, and reconstructs to form facets. Evidence for facet formation is based on a combination of LEED and STM studies.

When Pt is deposited onto W(111) at 300K, no distinct new features are seen in LEED; the background increases and the substrate spots become less sharp. When the surface is covered with $>1.1 \times 10^{15}$ Pt atoms/cm^2 and heated in the range 800 to 1600K, the LEED observations are very different: LEED beams appear which can be identified with the formation of microscopic facets. A characteristic of LEED from a faceted surface is the fact that LEED beams do not converge on the specular (0,0) beam from the originally planar surface as the kinetic energy increases. Rather, beams appear to converge on the specular (0,0) beams for the facets formed. For the present case, the beams converge on specular beams reflected from facets having W(211) orientation. Moreover, the beams are sharp and well-defined, indicating that the average facet dimension is ~100 Å.

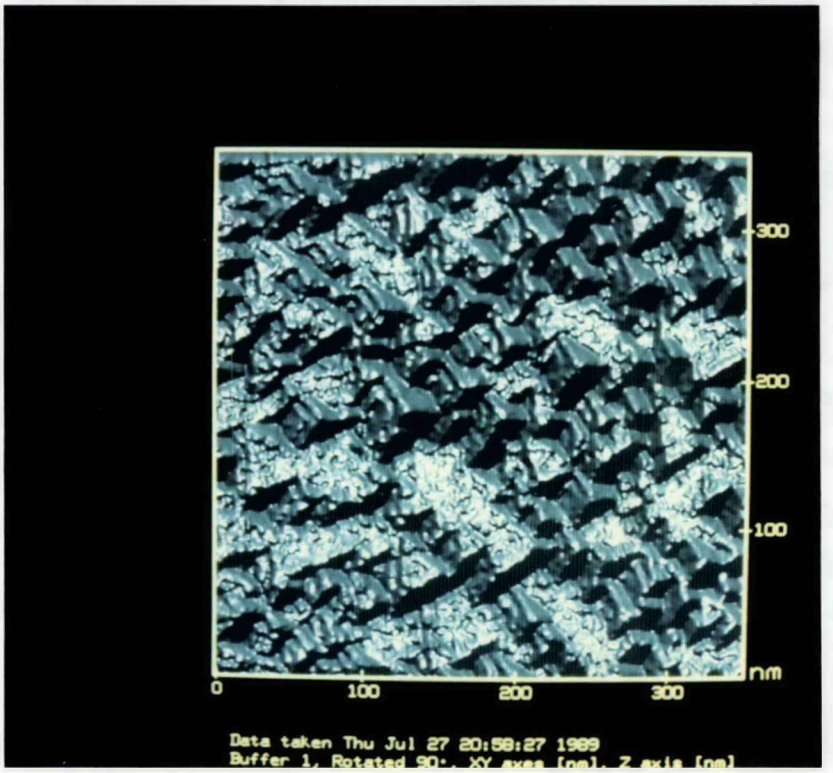

Figure 2
Scanning Tunneling Micrograph of Pt-induced faceting of W(111). The facets form after annealing of Pt-covered W(111) to 1200K in vacuum.

An STM image of the faceted W(111) surface is shown in Figure 2. For this experiment, the clean W(111) surface was dosed with several monolayers of Pt and heated under uhv conditions to 1200K. After removal from the vacuum system, it was transported to Professor Garfunkel's laboratory for STM characterization. Figure 2 shows a number of pyramidal facets having average dimensions of order 100 Å. All scans over different regions of the surface show similar results; the surface is completely covered by such pyramidal facets. In contrast, the back side of the crystal that was not dosed with Pt remains planar at the Angstrom scale: there is no massive reconstruction of W(111) upon heating in the absence of Pt.

Detailed LEED studies of Pt on W(111) are underway. We have found recently that, under certain conditions of Pt coverage and annealing temperature, the (211) oriented facets become faceted further to the (110) orientation. The temperature and Pt-coverage range necessary for the (211) to (110) transition are currently under investigation. Kinetics of facet growth are monitored with LEED using a Faraday cup assembly. Complementary measurements of the thermal desorption of Pt from W(111) are being correlated with the LEED studies.

d. Discussion

We believe that the observation of Pt-induced faceting on W(111) may have far-reaching implications for structural effects in bimetallic catalysts. Until the present most studies of metals-on-metals have been for

atomic close-packed substrates (bcc (110), fcc (111), (100)) which do not exhibit faceting. However small catalyst particles with high defect concentration may well undergo structural rearrangements to new shapes which are different for particles coated with other metals than for "clean" metallic particles.

We are very encouraged by the direct views of surface structural modification that are provided by using the STM. Note that we have not yet pushed the STM to the limit of atomic resolution. We are using it as a high resolution ($\lesssim$ 10 Å) scanning instrument that provides resolution more than an order of magnitude higher than the best scanning electron microscopes. Even at this level, we are resolving structural features not seen before at this magnification.

e. References

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3. Future Plans

Our objective is to study the relations between structure and reactivity in ultrathin films of metals on metals. We will focus on the morphology of potentially "unstable" surfaces which undergo massive reconstruction (faceting) upon annealing. Plans for the next several years are described in a renewal proposal. In brief, we plan to

a. Examine the thermal stability and growth characteristics of Pt on close-packed and rough, open W surfaces (W(110), (111), and (112)) addressing several issues, including the kinetics of facet formation, and the fate of "excess" Pt (i.e., > 1 ML), using LEED and STM as the major probes.

b. Determine the relation between structure and reactivity in chemisorption and catalysis on these surfaces, searching for unusual behavior (as for CO/Pt-W(110)). Systems will include adsorption of CO, O_2, C_xH_y..., and model catalytic reactions such as ethane hydrogenolysis in a UHV high-pressure reactor. What is the role of oxygen, hydrogen, CO, C, in faceting and clustering?

c. Identify other candidate substrates and overlayers for study of structure and reactivity in ultrathin films, based on practical or theoretical considerations (e.g., lattice match, electronic structure differences, previous work, segregation, or alloy formation). Candidate systems will include bcc (111), fcc (210), etc. Possible combinations include Cu/Ru, Cu/Ni, Pt/Re, W/Pt.

4. Personnel

The principal investigator moved from NIST to Rutgers as the State of NJ Professor of Surface Science in the autumn of 1988; he holds a joint appointment in the Depts. of Physics and Chemistry. He established this research activity with apparatus brought, in part, from NIST. The postdoctoral fellow and graduate students working on this activity have been steadily gaining expertise and familiarity with the apparatus and the science involved. The personnel are:

Professor Theodore E. Madey, Principal Investigator

Dr. Jack Ker-Jar Song, Postdoctoral Fellow (Ph.D. 1989, U. of Pennsylvania)

Mr. Cheng-Zhi Dong, Graduate Student (Physics)

Mr. Jei Guan, Graduate Student (Chemistry)

5. Publications

Papers published or prepared during this contract period include:

(a) "The Interaction of Oxygen and Platinum on Tungsten (110)", R. A. Demmin and T. E. Madey, J. Vac. Sci. Technol. A7, 1954 (1989).

(b) "Faceting Induced by an Ultrathin Film: Pt on W(111)", K.-J. Song, R. A. Demmin, C. Z. Dong, E. Garfunkel, T. E. Madey, Surface Science Letters, submitted.

(c) "Kinetics and Structure in Faceting of W(111) Induced by Pt and Oxygen", K.-J. Song, C.-Z. Dong, J. Guan, E. Garfunkel and T. E. Madey, in preparation.