AD-A123 734 STUDIES OF ADATOM-ADATOM INTERACTIONS IN CHEMISORBED LAYERS(U) WISCONSIN UNIV-MADISON M G LAGALLY 30 DEC 82 N00014-76-C-0727 1/1

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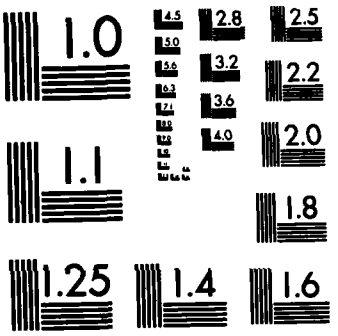

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N00014-76-C-0727-Final	2. GOVT ACCESSION NO. AD-A123 734	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) STUDIES OF ADATOM-ADATOM INTERACTIONS IN CHEMISORBED LAYERS		5. TYPE OF REPORT & PERIOD COVERED Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. G. Lagally		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0727
9. PERFORMING ORGANIZATION NAME AND ADDRESS Board of Regents of the University of Wisconsin System, 750 University Avenue, Madison, WI 53706		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 392-014
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		12. REPORT DATE December 30, 1982 13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Office of Naval Research Branch Office Chicago 536 S. Clark Street, Room 286 Chicago, IL 60605		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Surfaces, chemisorbed layers, phase transitions, low-energy electron diffraction.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-LF-014-6601

OFFICE OF NAVAL RESEARCH

Contract No. N00014-77-C-0474

Project No. 322-072

FINAL REPORT

STUDIES OF ADATOM-ADATOM INTERACTIONS IN CHEMISORBED LAYERS

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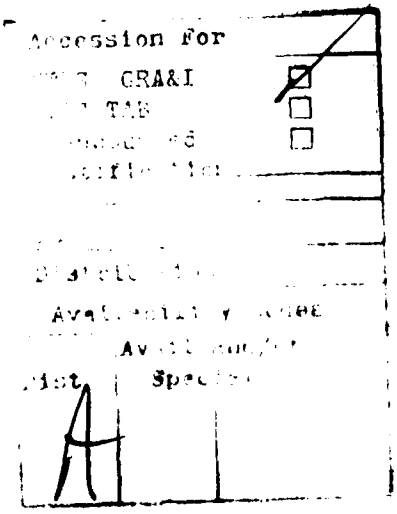
Abstract

Phase transitions in adsorbed layers have been studied both theoretically and experimentally, using low-energy electron diffraction (LEED) as the major technique. The model system O/W(110) was studied and its phase diagram determined. In particular, it was shown that a two-phase coexistence region must always exist if there is a net overlayer cohesive energy. The details of this coexistence region were investigated, including the influence of finite-size effects in the overlayer on the phase transition.



Introduction

The interactions between adsorbed species on a surface are ultimately responsible for a host of surface chemical phenomena. One approach to understanding the interactions between adsorbed species is through the study of the thermodynamics of model chemisorption systems. Clearly if the thermodynamics of the system are accurately known, one can formulate microscopic models and fit these to the data to extract quantitatively the various contributions to the adatom interactions. The most direct "picture" of the thermodynamics of a system is its phase diagram, a multidimensional plot of the chemical potential as a function of other thermodynamic variables, such as temperature, volume, pressure, and for multicomponent systems, the concentration of each component. For overlayer systems, the latter variable translates to coverage. For the study of overlayer phase diagrams, the most useful information is obtained from temperature-coverage phase diagrams. A fit to the phase boundaries of such a diagram will help establish the force law governing adatom interactions, which for chemisorption systems, because of the substrate-modulated oscillatory interaction, has been difficult to establish from first principles.

A number of experimental techniques have been applied[1-5] in the study of the thermodynamics of adsorbed layers, the majority, however, only on physisorption systems. Low-energy electron diffraction (LEED) appears to be the most fruitful technique for the study of chemisorbed

overlayer phase changes,[6-13] because the effect of adatom interactions is easily observed in the structure of the overlayer, and in variations of the structure with coverage, temperature, and substrate conditions. Thus for chemisorption systems superlattice structures that are some multiple of the substrate periodicity appear at temperatures sufficiently low so that $E_{A-A} > kT$. This manifests itself in superlattice LEED beams. It is the study of these beams that allows in many cases the determination of the overlayer phase diagram and thus the various contributions to adatom interactions. The necessary measurements include the temperature dependence of the superlattice beam intensities at various coverages and the measurement of the angula rofile of the diffracted beams. The phase boundaries can be extracted from the decay of the intensity with temperature. In addition, the angular profile gives information on the transition temperature and the influence of substrate defects or finite-size effects on the phase boundaries.

From the phase boundaries it is then possible theoretically to extract adatom interactions, after choosing a model for the interaction energy terms required. Additional theoretical effort is required in intepreting the angular profiles in terms of finite-size effects.

Research Accomplished Under This Contract

We have concentrated our research on one model system, O/W (110), that incorporates some of the best aspects of two-dimensional phases. It is a closed system, i.e., the adsorbed overlayer does not interact with the bulk in the temperature range that is of interest in investigating the adatom interactions, and its binding energy to the substrate

is so large and as a result its vapor pressure is so low in the temperature range of interest that there is effectively no interaction with the gas phase, either. Hence it is a system that is a lattice gas at constant coverage over a wide temperature range. This has made it ideal for study, not just for the sake of the adatom interactions in this system itself, but for testing experimental techniques and theoretical methods that will be applicable to more complex chemisorption systems and surface chemical reactions. Experimental results from this system have given us the impetus to analyze more closely exactly what it is one can learn, what it is that LEED can measure or not measure, what the effect of substrate surface or overlayer conditions is on the thermodynamic properties of the overlayer, and how all of these affect a determination of adsorbate interaction energies.

The major results obtained during the life of this contract are:

1. LEED Measurements of the Disordering and Ordering of O on W(110) Surfaces.

In these measurements[9,11], the temperature dependence of the diffracted beams is measured. The temperature at which the peak intensity either disappears or goes through an inflection point (depending on the phase region[14]) is plotted. From these measurements, the phase diagram can be drawn.[14] The most interesting conclusion of these measurements is that, if there is a net attractive interaction between adatoms[9,11,14], these must always be a two-phase region at

sufficiently low coverages and temperature, consisting of ordered two-dimensional islands and nearly empty substrate lattice.

2. Theoretical Analysis of Coexistence Region

The coexistence region, consisting of islands and "sea" has a boundary that depends on the adsorbate interactions. In simple cases, this can be modeled with the lattice gas formulation of Lee and Yang[15]. This was done for O on W(110) and a interaction energy of 0.07 eV/atom extracted.[16] Monte-Carlo modeling[17] and further theoretical analysis placing limits on the interactions was also performed.[18]

3. Influence of Finite-Size Effects on the Phase Diagram

By measuring the LEED angular profiles, it is possible to extract the average size of islands that form on the surface. In principle, for thermodynamic equilibrium on perfect substrates, the sizes of these islands should be so large as to be unmeasurable with common LEED instruments. This was not the case for O on W(110). The substrate perfection was measured[19] and determined to be rather poor, with a step density of 1.7%, i.e., an average terrace size of 60 atoms. The resultant overlayer island sizes were measured as a function of coverage.[14] A comparison of these sizes with sizes that would be expected on the basis of the phase diagram (which assumes that there are no finite-size effects) indicates that finite- size effects cause a contribution to the free energy of the islands that makes them less stable.[14]

4. Other Results

A number of other results were obtained. These are most directly reviewed by reference to the list of publications prepared under this contract, in particular numbers 9, 11, 12 and the dissertations numbered 14 and 15.

List of Publications

1. "Island-Dissolution Phase Transition in a Chemisorbed Layer", T. M. Lu, G.-C. Wang, and M. G. Lagally, Phys. Rev. Letters 39, 411 (1977).
2. "Monte-Carlo Modeling of Phase Changes in the Chemisorption System O/W (110)", W.-Y. Ching, D. L. Huber, M. Fishkis, and M. G. Lagally, J. Vac. Sci. Technol. 15, 653 (1978).
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4. "Chemisorption: Island Formation and Adatom Interactions" M. G. Lagally, G.-C. Wang, and T.-M. Lu, CRC Critical Reviews in Solid State and Materials Sciences 7, 233 (1978).
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7. "Island Formation and Condensation of a Chemisorbed Overlayer", T.-M. Lu, G.-C. Wang, and M. G. Lagally, Surface Sci. 92, 133 (1980).

8. "Surface Defects and Thermodynamics of Chemisorbed Layers", M. G. Lagally, T.-M. Lu, and D. G. Welkie, J. Vac. Sci. Technol. 17, 223 (1980).

9. "Adsorbed-Overlayer Critical Phenomena by Low-Energy Electron Diffraction", T.-M. Lu, in Ordering in Two Dimensions, ed. S. Sinha, Elsevier (1980).

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14. "Quantitative Island size Determination and Phase Transitions in a Chemisorbed Oxygen Layer on W(110)", G.-C. Wang, PhD dissertation, University of Wisconsin-Madison (1978, unpublished).

15. "Quantitative Analysis of Extended Defects at Surfaces Using Low-Energy Electron Diffraction", D. G. Welkie, PhD dissertation, University of Wisconsin-Madison (1981, unpublished).

Persons Supported Under This Contract

G.-C. Wang

T.-M. Lu (part)

D. G. Welkie (part)

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