FIELD ION MICROSCOPY

A Final Report to the

OFFICE OF NAVAL RESEARCH

Contract Nonr-656 (23)

June 1959 - May 1969

Field Emission Laboratory
Department of Physics
The Pennsylvania State University
University Park, Pennsylvania

Erwin W. Mueller, Principal Investigator

Final Report

June 1, 1959 to May 31, 1969

Office of Naval Research

Contract Nonr-659 (23)
NR 017-443

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Introduction

The Field Emission Laboratory has been supported by the Office of Naval Research since 1959. Over the past ten years the annual contribution of this contract, Nonr-656 (23), amounted to between 30% and 15% of the laboratory's total operation. The present report summarizes the work done under the ONR contract, lists the publications that have resulted from the work and reports the names of the academic personnel involved in the project.

Summary of Scientific Accomplishments

The objectives of this research have been the development of improved field ion microscopes (FIM), a more complete understanding of the physical principles involved, and the application of the instrument to some specific problems in the physics of surfaces and the properties of metals. The FIM had been conceived by the principal investigator in 1951 and developed to full atomic resolution in 1956. By the time of the beginning of the present ONR contract in 1959, the potential applications had been demonstrated with the imaging of more than a dozen of different metals. At that time, The Penn State Field Emission Laboratory was essentially the only place where field ion microscopy was practiced. (A small group under M. Drechsler, left behind by the principal investigator in his former laboratory at the Max-Planck Institute in Berlin, contributed some work on tungsten). During the present decade, the FIM became gradually an accepted tool in physical metallurgy and surface physics. All of the important techniques, with the exception of Moore's computer simulation (A. J. W. Moore, J. Phys. Chem. Solids 23, 907 (1962)), have been pioneered in the Penn State Field Emission Laboratory. The results that have emerged from the present contract are described in twenty-five publications. They are listed in the bibliography given below, and the reference numbers in the text of this report refer to relevant papers. Of these publications, seventeen have also been distributed as Technical Reports. At the annual Field Emission Symposia held at various places in the U.S. and twice in Europe, a total of twenty ONR supported papers were presented by our group. Abstracts of these are recorded in the programs of the meetings. The titles of these papers are also listed below as references 26 to 45.

In the initial efforts of this research, we tried to overcome a basic disadvantage of the FIM, its extremely low image intensity. Successful approaches were the dynamic gas supply[2] and the use of an external photo-electronic image intensifier[4,5,29]. With both techniques it became possible to obtain a cinematographic recording[31] of the field evaporation process and the emergence of lattice defects at the surface.

Another method of increasing the image brightness was introduced using partial shielding of the tip[10] to increase the acceleration voltage of the imaging ions.

In the area of image intensification, a considerable progress has recently been achieved in Cambridge, England by ion-electron image conversion using secondary emission from fine wire meshes or in channel plates. Unfortunately, we were unable to participate in this development due to budgetary limitations: Our total equipment budget for the years since 1963 amounted to $640. For this reason we also had to terminate prematurely our original development of a versatile metal FIM[3,27]. Fortunately, we were able to design a much more advanced instrument with NSF funds, which was used for the ONR contract work for in-situ manipulation of specimens[15] and several other investigations.

Because of our inability due to budget limitations in pursuing the image itensification problem, we looked for other means of improving the usefulness of the FIM. Immersion of the entire FIM in a liquid hydrogen cryostat[17] and the measurement of current-voltage characteristics by photometry[14], were part of the effort to advance the understanding of the image formation process. The observation of x-rays and of charge exchange[38] in the FIM also contributed in this direction.

A surprising observation was made with the measurement of the energy distribution in field ionization[6,32] by a retarding potential technique when it turned out that the half-width of 0.8 eV indicated the origin of the imaging helium ions to lie within a disc of not more than 0.2 Å thickness floating about 4 Å above the imaged surface atom. To this unexpectedly sharp localization of the ion's origin, we soon added another observation which at first seemed to be impossible to understand with the accepted mechanism of tunneling of an electron from the ground state of the helium atom into the top of the conduction band of the metal. While the field ordinarily required to ionize helium is 450 MV/cm, the adsorption at the metal surface of hydrogen reduced that field to 300 MV/cm[8,12,13,33]. The explanation of this novel effect of hydrogen promotion of field ionization was finally found in the rearrangement of surface charge (E. W. Müller, Surface Sci. 8, 462 (1967)) which occurs when atomic hydrogen is adsorbed in the interstices of sufficiently loosely packed net planes of the metal surface and attracts an electron from an adjacent metal atom to form a hydride-like bond. As a result the metal atom assumes an increased positive charge density and thereby enhances the externally applied field sufficiently to field-ionize the helium image gas atom. The practical advantage of this process is the possibility of imaging a non-refractory metal that ordinarily would field-evaporate at 450 MV/cm at a greatly reduced field strength, while still maintaining the excellent resolution of a helium ion image[12,13]. The addition of hydrogen also promotes field evaporation of metals, and a delicate balance must be found to utilize the promotion of field ionization without increasing the evaporation rate too much. Complex field induced corrosion effects may develop in some cases[23]. Hydrogen promotion is now the generally accepted technique for imaging non-refractory metals such as iron, nickel, cobalt, copper and gold.

The proper interpretation of hydrogen promotion of field ionization was only possible after our discovery of the invisibility of cobalt atoms in an ordered Pt-Co alloy[16,18]. This investigation was originally undertaken because due to the known arrangement of two constituents of the ordered alloys it offered an opportunity of comparing the imaging properties of different atoms. It was now realized that the electronic properties of the surface metal atom is more important than its geometrical position in the surface. The electric field above an adsorbate atom may also be much different from that above the substrate atoms. Thus the limits of the naive image interpretation of geometrical local field enhancement, as expressed in a refined form in the Moore computer model, have now been greatly expanded by including the possible charge rearrangement due to alloy constituents or chemisorbed species. The effects of surface states and of the polarization of the surface atoms upon field ionization and field evaporation[20,21,25] are now more clearly seen.

Although our main interest was centered around the development of the FIM and the increased understanding of the physical effects involved, we have also made some efforts towards applications in physical metallurgy. Direct observation of lattice defects[1] is the most important capability of the FIM. Utilizing its unique atomic resolution, we were the first to investigate a grain boundary in atomic details[26]. Studies of the initial oxidation of tantalum[11] revealed the diffusion behavior of oxygen interstitials. We observed some unknown interstitial impurities in rhodium[36], while laser-pulse heating of specimen tips[15,37] produced vacancy clusters, voids, and in iridium a disk like oxygen precipitate.

Considerable efforts were made to investigate the structures of fully and partially ordered Pt-Co and Pt_3-Co alloys[16,18,19,22,24,40,42]. Image structures of domains, such as 90-deg orientation domains, antiphase domains and order-disorder domains, are readily identifiable. We found that most of the former interpretation of domain image structures by the Cambridge group was wrong. We were also able to investigate the ordering mechanism of the alloys by annealing of the specimens. Sharp boundaries between the ordered and the disordered phases were directly visible for the first time. We also showed that the ordering parameters, such as the degrees of long range and short range order can be obtained from field ion micrographs. As an example, we calculated the long range order parameter S for a Pt_3-Co sample to be 0.95 from a counting of the misplaced atoms.

It is quite clear that in field ion microscopy of ordered binary alloys, the techniques for further studies are now well established from our investigation of the platinum-cobalt alloys. What is mostly needed now are advances in the understanding of the field evaporation process. Since the discovery of this basic physical effect in our laboratory and the introduction of the image force theory of field evaporation (E. W. Müller, Phys. Rev. 102, 618 (1956)), some progress has been made[9,20,25,41,45], but we do need more experiments as well as an advanced theory since our latest surprising results obtained with the novel Atom-Probe FIM (conceived by the principal investigator in 1967 and developed in this laboratory under an NSF grant). We now know that many metals evaporate as three and four fold charged positive ions (E. W. Müller, J. A. Panitz and S. B. McLane Rev. Sci. Instr. 39, 83 (1968)) at rates up to 10^9 layers/sec, and that helium and neon image gases are field adsorbed at the emitter surface at temperatures as high as 78° K and thereby affect seriously the field evaporation process (E. W. Müller, Quarterly Rev. 23, 177 (1969), E. W. Müller, S. B. McLane and J. A. Panitz, Surface Sci. November 1969). Clearly, a large unexplored area of surface physics and high-field effects of gas-surface interactions has been uncovered by the past research, and must be investigated in the future.

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2. Operation of the FIM with a Dynamic Gas Supply. B. J. Waclawski and E. W. Müller. J. Appl. Phys. 32, 1472 (1961) Technical Report No. 2

3. A Versatile Field-Ion Microscope. S. B. McLane and E. W. Müller, 1963. Technical Report No. 3

4. Use of an Image Intensifier for Field-Ion Microscopy. S. B. McLane and E. W. Müller. Bull. Am. Phys. Soc. Ser. II 8, 431 (1963).

5. Field-Ion Microscopy with an External Image Intensifier. S. B. McLane, E. W. Müller and O. Nishikawa, Rev. Sci. Instr. 35, 1297 (1964).

6. Measurement of the Energy Distribution in Field Ionization. T. T. Tsong and E. W. Müller, J. Chem. Phys. 41, 3279 (1964). Technical Report No. 4

7. Progress and Limitations in Field-Ion Microscopy. E. W. Müller, Internat. Conf. on Materials, ASTM, Phila., 1964. p. 420.

8. Gas Surface Interaction and Field-Ion Microscopy of Non-Refractory Metals. E. W. Müller, S. Nakamura, O. Nishikawa and S. B. McLane. J. Appl. Phys. 36, 2496 (1965) Technical Report No. 5

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10. Increased Image Brightness in a FIM. E. W. Müller and O. Nishikawa. Rev. Sci. Instr. 36, 556 (1965).

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13. Controlled Hydrogen Partial Pressure in a FIM. E. W. Müller, S. Nakamura, S. B. McLane and O. Nishikawa. Trans. Third Internat. Vacuum Congr. Stuttgart 1965, Pergamon Press, Oxford 1966. Vol. 2 p. 431.

14. Current-Voltage Characteristics by Image Photometry in a FIM. T. T. Tsong and E. W. Müller. J. Appl. Phys. 37, 3069 (1966) Technical Report No. 9

15. In-Situ Manipulation of FIM-Specimens. E. W. Müller, S. B. McLane and O. Nishikawa. Proc. Sixth Internat. Congr. Electron Microscopy, Kyoto 1966. Vol. 1, p. 235. Technical Report No. 10

16. The Field-Ion Microscopical Image of an Ordered Pt-Co Alloy. T. T. Tsong and E. W. Müller. Appl. Phys. Letts. <u>9</u>, 7 (1966) Technical Report No. 11

17. Increased Image Brightness by Immersion of a FIM. E. W. Müller. J. Appl. Phys. <u>37</u>, 5001 (1966). Technical Report No. 12

18. Domain Structure of Ordered Equiatomic Pt-Co Observed in the FIM. T. T. Tsong and E. W. Müller, J. Appl. Phys. <u>38</u> 545 (1967) Technical Report No. 13

19. Ordered Pt_3-Co Alloy Studied in the FIM. T. T. Tsong and E. W. Müller, J. Appl. Phys. <u>38</u> 3531 (1967) Technical Report No. 14

20. On the Mechanism of Field Evaporation. T. T. Tsong, Surface Sci. <u>10</u>, 102 (1968). Technical Report No. 16

21. Surface States and Field-Ion Image Formation. T. T. Tsong, Surface Sci. <u>10</u>, 303 (1968). Technical Report No. 15

22. Domain and Phase Boundaries of Pt-Co Alloys Observed in the FIM. T. T. Tsong and E. W. Müller, Proc. 4th European Regional Conf. Electron Microscopy, Rome 1968, Vol. 1, p. 443.

23. Hydrogen and Hydrogen-Neon Promoted Field Ionization of Helium. O. Nishikawa and E. W. Müller, Surface Sci. <u>12</u>, 247 (1968).

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25. Effects of Static-Field Penetration and Atomic Polarization on the Capacity of a Capacitor, Field Evaporation and Field Ionization Processes. T. T. Tsong and E. W. Müller, Phys. Rev. 181, 530 (1969) Technical Report No. 17

Papers Supported from Contract Nonr-656 (23)

Presented at the Annual Field Emission Symposia:

26. A Study of a Grain Boundary in Three Dimensions. S. B. McLane and E. W. Müller, 9th FE-Symp. Notre Dame, 1962.

27. A Versatile Field-Ion Microscope. S. B. McLane and E. W. Müller, 9th FE-Symp. Notre Dame, 1962.

28. Current-Voltage Characteristics in the He-Ion Microscope. E. W. Müller and F. I. Mann. 10th FE-Symp. Berea, Ohio 1963.

29. Image Intensifier Field-Ion Microscopy, S. B. McLane and E. W. Müller, 10th FE-Symp. Berea, Ohio 1963.

30. Field-Ion Microscopy with Neon. O. Nishikawa and E. W. Müller, 10th FE-Symp. Berea, Ohio 1963.

31. Motion Picture Observations with the FIM. E. W. Müller, S. B. McLane and Nakamura. 11th FE-Symp. Cambridge (England) 1964.

32. Measurement of the Energy Distribution in Field Ionization. E. W. Müller and T. T. Tsong. 11th FE-Symp. Cambridge (England) 1964.

33. Gas-Surface Interaction in the FIM. E. W. Müller, S. Nakamura, O. Nishikawa and S. B. McLane. 12th FE-Symp. Penn State University 1965.

34. Field and Temperature Dependence of the Image Brightness in a FIM. T. T. Tsong and E. W. Müller. 12th FE-Symp. Penn State University 1965.

35. Elastic Deformation of Emitter Tips by the Imaging Field. E. W. Müller, K. Rendulic and S. Nakamura. 12th FE-Symp. Penn State University 1965.

36. Impurity Interstitials in Tantalum and in Rhodium. E. W. Müller, S. Nakamura, K. Rendulic and S. B. McLane. 12th FE-Symp. Penn State University 1965.

37. Laser Pulse Heating of Emiter Tips. E. W. Müller and S. B. McLane. 12th FE-Symp. Penn State University 1965.

38. Remarks on the Resolution, the Occurrence of Charge Exchange and of X-Rays in the FIM. E. W. Müller. 13th FE-Symp. Cornell University 1966.

39. FIM Study of NbN. T. T. Tsong and E. W. Müller. 13th FE-Symp. Cornell University 1966.

40. FIM Study of the Equiatomic Pt-Co Alloy. T. T. Tsong and E. W. Müller. 13th FE-Symp. Cornell University 1966.

41. The Mechanism of Field Evaporation. T. T. Tsong. 14th FE-Symp. Washington D.C. 1967.

42. FIM Study of Pt_3-Co. T. T. Tsong and E. W. Müller. 14th FE-Symp. Washington, D.C. 1967.

43. Static Field Penetration and Atomic Polarization at a Metal Surface. T. T. Tsong and E. W. Müller. 15th FE-Symp. Bonn, Germany 1968.

44. Localized Surface Disorders by Hydrogen-Neon Image Gas. O. Nishikawa and E. W. Müller. 15th FE-Symp., Bonn 1968.

45. Further Discussion of Field Evaporation. T. T. Tsong and E. W. Müller. 16th FE-Symp. Pittsburgh 1969.

Personnel

During the period of this report the following academic personnel have been associated with the project:

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Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Department of Physics, 205 Osmond Lab. The Pennsylvania State University University Park, Pennsylvania 16802	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Field-Ion Microscopy

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Final Report, June 1959 - May 1969

5. AUTHOR(S) (First name, middle initial, last name)

Erwin W. Mueller, Evan-Pugh Research Professor of Physics

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
30 September 1969	12	45

8a. CONTRACT OR GRANT NO. Nonr-656 (23) b. PROJECT NO. c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Office of Naval Research

13. ABSTRACT

The objectives of this project include the development of improved field-ion microscopes, several means of image intensification, and experiments to clarify the physical processes of ion image formation. Applications of field ion microscopy to the study of lattice imperfections and to order-disorder structures of Pt-Co alloys are described. A bibliography containing twenty-five publications and twenty presentations at the annual Field Emission Symposia is given, and the academic personnel connected with this work is listed.

DD FORM 1 NOV 65 1473 (PAGE 1)
S/N 0101-807-6811

Unclassified
Security Classification

A-31408