FIELD-ION MICROSCOPY

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FIELD-ION MICROSCOPY

Dedicated to

Professor Erwin W. Müller

by his coauthors for his overwhelming contributions to the theory and practice of field-ion microscopy.

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PREFACE

The short course on Field-Ion Microscopy held at the University of Florida, Gainesville, Fla., Mar. 14–22, 1966, whose lectures comprise this volume, was intended to be a means of assembling and making accessible the information essential to a research group just taking up field-ion microscopy. As a consequence, the present chapters do not read like the usual proceedings of a symposium but rather somewhat like a graduate-level textbook. Insofar as is possible when there are eight authors, this is exactly what is intended. Not all of the presently known applications of the technique are treated with equal thoroughness, but we hope none has been neglected. The closely related subject of field-electron emission has been given only a cursory treatment here, since other comprehensive treatments on this subject are available.

Although it may be unusual, the other seven authors would like to dedicate this book to their coauthor, Professor E. W. Müller. Inventor of field-electron-emission microscopy and field-ion microscopy and the most important contributor to both fields for many years, Professor Müller still possesses the eagerness, imagination, and drive of a fledgling Ph.D. To observe this personally, one need only attend the annual Field-Emission Symposium. We salute this remarkable scientist.

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Chapter 1

THE THEORETICAL AND TECHNICAL DEVELOPMENT OF FIELD-ION MICROSCOPY

E. W. Müller†

1.1 Early Historical Development

A field-ion microscope is the most powerful microscopic device known today. It is the only instrument that can show directly the atomic structure of a specimen and the atomic lattice defects. But, for reasons that might lie in the difficulty of operation of the first instruments, perhaps the unorthodoxy of the principles involved, and a justified lack of commercial interest, it took a long time to be developed. When in the spring days of quantum mechanics Gamow[1] (1928) explained the radioactive alpha decay as a tunneling effect, field-electron emission from metals was soon recognized by Fowler and Nordheim[2] as another example of barrier penetration and simultaneously Oppenheimer[3] suggested that the effect of field ionization of free atoms could occur when an electron would tunnel out in the presence of an electric field. While the first two effects commanded considerable interest, field ionization from the ground state of an atom was experimentally inaccessible because of the magnitude of the fields required. Handling large fields became a possibility with the introduction of the field-emission microscope in 1936.[4] With the discovery of field desorption[5] from a positive-point electrode the field range beyond 100 MV/cm, in which all effects of interest to us are taking place, was entered for the first time. The realization that the resolution limit of the field-electron microscope[6] is determined by the tangential velocity of the emitted electrons and, to a lesser extent, by their de Broglie wavelength, which cannot be controlled under the prevailing conditions, led in 1951 to successful imaging of the emitter surface with positive ions rather than electrons.[7] Atomic resolution was thus achieved for the first time. The imaging ions were first thought to originate from an intermediate adsorbed

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state, although true field ionization of hydrogen at higher fields in free space was clearly recognized to occur in these early experiments.

Details of the further development of field-ion microscopy since its inception will be more profitably discussed in later sections in connection with the various specific problems involved. It appears that the general development proceeded in steps some 5 years apart. In 1955 to 1956 the significance of accommodating the image gas atoms to the tip temperature had been realized and led immediately to the operation of the microscope at cryogenic temperatures.[8] Fortunately at the same time the further pursuit of the field desorption process led to the discovery of field evaporation[9] which is next to field ionization the most significant physical effect on which field-ion microscopy is based.†

The concept of hopping image gas molecules, introduced in 1956,[10] turned out to be fruitful for all further theoretical considerations as well as the immediate improvements of the imaging procedures. Only at this stage was true atomic resolution of large sections of the specimen achieved. Direct visualization of the atomic crystal lattice and its defects was a reality. Vacancies, interstitials, and impurity atoms were seen as individual entities, and dislocation cores, slip bands, and cold-worked structures were revealed in intimate detail. By 1960 most of the present day experimental techniques were developed or initiated to give high-quality images of the lattice defects. Only then, perhaps helped by the appearance of a first detailed description of the principles and techniques involved,[11] did field-ion microscopy begin to be taken up seriously at various other places outside the laboratory of the author. During the last 5 years progress was made in the refinement of the theory,[12–14] in the more general recognition of the possibilities and limitations of the technique,[15] and in the increasing application of this research tool in electron physics of surfaces, in physical metallurgy, and potentially in molecular biophysics.

1.2 Basic Principles of the Field-Ion Microscope

The microscope was developed from its forerunner, the field-electron microscope,[4] which in its simplest form consists of the metallic specimen shaped to a finely pointed needle tip as a cathode and opposite to it a fluorescent screen as an anode, both mounted in a highly evacuated glass tube. With sufficient applied voltage, the field at the emitter reaches 30 to

† The term *field evaporation* and numerical data for room-temperature evaporation are mentioned in M. Drechsler and G. Pankow, *Proc. Intern. Conf. on Electron Microscopy, London*, 1954. However, these items were not presented at this conference, but were added to the proof after Dr. Drechsler had received a preprint of the *Phys. Rev.* article[9] in Sept., 1955. The *Proceedings* appeared late in 1956.

50 MV/cm, and the electrons tunneling out in normal direction to each surface element of the hemispherical tip cap radially project the specimen surface onto the fluorescent screen. The magnification is approximately equal to the ratio of screen distance to tip radius and can easily be made a million diameters, while the resolution limit is about 25 Å.

In the field-ion microscope the essential features are the same, but this time the specimen tip is usually of a smaller radius and kept at a higher, positive potential to produce a field of the order of magnitude of 500 MV/cm. The image information is carried from the tip surface to the screen by radially projected positive ions. The magnification is up to several million diameters, and the resolution often between 2 and 3 Å. The ions are not emitted from the specimen but are produced in its immediate proximity[16,17] by field ionization of the imaging gas which is introduced into the microscope tube at a pressure of a few millitorr, low enough to provide sufficient free path to let the ions travel to the screen without disturbing collisions. Two quite basic technical details are the provision for cooling the tip by heat conduction through its leads from a "cold finger" filled with a cryogenic liquid,[8] and a flat screen, which is required for photographing the weak images with a high aperture objective having a small depth of focus. A kind of heat shield around the tip, usually at screen potential, not only cools the gas arriving at the tip but also serves simultaneously as a means of restricting the volume containing the electric field, which is a useful design detail in a gas-filled high-voltage tube.[18] Another important technical detail in the early development was the use of a demountable microscope which allowed easy and fast tip replacements. Without this scheme, which with He or Ne as imaging gases still ensures atomically clear surfaces in spite of modest vacuum conditions,[18] the exploration of the many possibilities of field-ion microscopy[11] would have been much slower.

Under proper operating conditions the applied voltage is chosen so that ionization occurs only in the exceptionally strong field regions above the protruding atoms of the specimen surface or above the approximately circular edges of closely packed net planes. Accelerated by the extremely high field normal to the hemispherical surface, each of its protruding atoms sends a narrow beam of ions to the screen. The angular width of the beam, mostly determined by the random lateral velocity component of the ions and changing inversely with the tip radius, is as narrow as $\frac{1}{10}$ of 1°. Thus the total ion image, typically encompassing about two-thirds of a hemisphere, can be quite sharp and finely detailed if a large tip radius, in practice up to 2000 Å, is used. On the other hand, since at low tip temperature the resolution does not improve much with a smaller tip radius, the images of small tips, having radii down to below 100 Å, appear quite blurred owing to their unnecessary overmagnification. Fairly independent of the tip radius is the strength of

the ion beam coming from a single surface atom, i.e., under practical conditions some 10^5 ions/sec or an ion current in the 10^{-14} A range.

As the specimen tip is simultaneously the image quality-determining "lens," some introductory remarks about shaping the tip are in order. Specimens are normally prepared from small cylindrical or rod-shaped samples, mostly in the form of fine wires, vapor-grown whiskers, or machined rods, by using chemical or electrochemical etching and polishing to form a conical needle shape ending in the extremely sharp point with dimensions well below the range of an optical microscope. In field-electron microscopy the technique of finishing the emitter to a high degree of perfection by annealing the tip was found to be most useful. At temperatures above one-half or two-thirds of the melting point, surface migration of most metals becomes fast enough to rearrange the surface, which then approaches a shape of minimum free surface energy. The resulting frozen-in annealed end form, consisting of flat low-index crystal planes connected by smoothly curved intermediate regions, is regular enough for the limited resolution of the field-electron microscope but not for the field-ion microscope. Certainly, field-ion microscopy would not have reached its present capabilities if the effect of field evaporation[9] had not been discovered as a means to prepare essentially perfect tip surfaces. In the field-ion microscope the field at a crudely prepared tip is made so high that metal atoms evaporate from the surface even at cryogenic temperatures. As the field is gradually increased, evaporation of the most protuberant asperities occurs first because of the exceedingly large local field. This process continues as long as the voltage is kept high enough, and results in a field evaporation end form which is atomically smooth and crystallographically as perfect as the bulk material of the specimen. Once the end form is established, field evaporation can be continued at a well-controlled rate, which gives a welcome opportunity to "dissect" the specimen to explore the internal structure by "bringing it to the surface" for inspection.

The original image force theory of field evaporation,[9] only just recently refined,[14] served as a useful guide for the selection of materials suitable for field-ion microscopy. By 1958 images of some 18 metals and of carbon had been observed,[18] and the possibility of increasing the list of materials by going to other imaging gases such as neon, hydrogen, and deuterium had been explored.[19] The development of the standard microscopical techniques was essentially accomplished with the introduction of *in situ* treatments of specimens, such as cathode sputtering, α-radiation, cyclic field stressing for fatigue studies, and field stressing at elevated temperatures to investigate yield phenomena.[11,18] The color printing technique[10] helped to pinpoint *in situ* surface changes. Taken together with the direct counting of vacancy concentration[20] and the imaging of defect structures containing slip bands

and twin boundaries,[21] the possibilities of field-ion microscopy as a tool for metallurgical research was clearly established by about 1960. Since then, detailed work has been taken up at a number of laboratories all over the world. Some of the recent advances in the author's laboratory are the concept of field-stabilized surface sites and their interpretation as artifacts,[15] the successful application of the image intensifier for cinematographic recording of transient helium and neon ion images of unstable surfaces,[22] and the practical use of hydrogen promotion for imaging the nonrefractory transition metals which resulted from a closer investigation of gas–surface interactions.[23]

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