The Archetypal Atom-Probe

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The ultimate microanalytical tool would be an instrument capable of selecting and identifying the individual constituents of a surface seen in atomic resolution. This daunting task is possible with a combination field ion microscope and mass spectrometer having single-particle detection sensitivity. The resulting device is called the *atom-probe*. With the atom-probe it is possible to identify a single atom seen on a metal surface and selected from neighboring atoms at the discretion of the observer.   © Elsevier Science Inc., 2000. All rights reserved.

PREFACE

In the Atom-Probe, as originally conceived, a surface species was imaged in a field ion microscope and selected for examination by positioning its image over a small aperture or *probe hole* in the microscope's fluorescent screen. The selected particle was removed from the surface as a positive ion by field evaporation, and traveled through the probe hole into a time-of-flight mass spectrometer. The time correlation between the ion's impact at a suitable detector, and the evaporation event itself allowed the ion's travel time to be determined with great precision. Because the ion's kinetic energy and travel distance are also well defined and accurately known, its mass-to-charge ratio can be determined with precision. This manuscript focuses on the first atom-probe by reproducing the first three chapters (Introduction, Theory of Operation, A Prototype Instrument) of the Ph.D. thesis that described the original instrument [1]. The original acknowledgment, the original references (beginning with reference 3), and the original figures (beginning with Fig. 3) are included.

Many variations of the atom-probe principle were developed after the original instrument was introduced (more than 30 years ago). Technical innovation has continued, but costs have escalated as well.

Figure 1 is a reproduction of the original award letter from the National Science Foundation. Notice that the total award for 24 months (including overhead) is $59,300. Figure 2 is a reproduction of the research budget. It included two senior personnel, six support personnel, equipment, travel, publication, and machine shop costs. Times have certainly changed. It is doubtful that the same level of effort could be completed today for less than five times the original budgeted amount!

INTRODUCTION

The field ion microscope, invented by Müller in 1951 [2], is the only instrument capable of resolving the individual atoms of a metal surface. In practice, each protruding surface atom of a specially prepared specimen is imaged on a fluorescent screen by a beam of ions, usually helium, formed some four angstroms above it in a narrow region of high ionization probability [3]. The image that is observed on the screen of the microscope is actually a highly magnified representation of these ionization regions. Because a one-to-one correspondence is present between each localized ionization region and the surface atom directly below it, the entire image represents the atomically resolved surface

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NATIONAL SCIENCE FOUNDATION

WASHINGTON, D.C. 20550

JUN 5 1967

Dr. Eric A. Walker, President
The Pennsylvania State University
University Park, Pennsylvania 16802   GP-7452
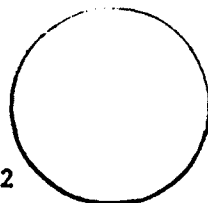
Dear Dr. Walker:

It is a pleasure to inform you that a grant of $59,300 is
awarded to The Pennsylvania State University for the sup-
port of research entitled "Atom-Probe Field Ion Microscope."
This research is to be under the direction of Erwin W.
Mueller, Department of Physics. It is effective June 1,
1967, for a period of approximately two years.

The Foundation requires that this grant be administered in
accordance with the conditions, policies, and procedures
stated in "Grants for Scientific Research," June 1963 (as
amended December 1963 and supplemented by Important Notice
of January 24, 1966), Enclosure R-8 (Rev. 9/66), and the
attached budget summary.

Please acknowledge acceptance of this grant under the above
terms and include in your acknowledgment a reference to the
grant number.

Sincerely yours,

John T. Wilson
Deputy Director

FIG. 1. The NSF award letter.

of the specimen. However, because this im-
aging process is similar for all surface at-
oms regardless of their chemical nature, it
is usually not possible to use the appear-
ance of the FIM image to directly discrimi-
nate between different atomic species at the
surface. Although it seems quite certain
that only one kind of atom is present on
pure W, Ir, Rh, or Pt surfaces characterized
by a highly perfect FIM pattern, it is not
possible to unambiguously identify the dif-
ferent atomic species forming the usually
less regular FIM patterns that are obtained
from alloys, crystals containing impurities,
or adsorbates at the surface. Fortunately,
the field ionization of an ambient gas upon
which the imaging process relies is not the
only observable effect due to the presence
of the high electric field near the surface. It
is, in fact, an associated process called field

TWENTY-FOUR MONTH BUDGET

		NSF Grant	Grantee Share
A.	SALARIES		
	Senior Personnel:		
	(1) Principal Investigator 15% time, calendar years	$ 8,070	$ -
	(2) Faculty Associate 25% time, calendar years	6,840	-
	Other Personnel:		
	(3) Research Associate 25% time, calendar years	4,860	-
	(4) Research Assistant 50% time, calendar years	6,960	-
	(5) Technician 20% time	2,880	-
	(6) Secretary 15% time	1,110	-
		$30,720	$ -
B.	PERMANENT EQUIPMENT	13,365	-
C.	EXPENDABLE EQUIPMENT AND SUPPLIES	5,075	-
D.	TRAVEL		
	Domestic	450	-
E.	PUBLICATION COSTS	800	-
F.	OTHER		
	(1) Machine shop	1,400	-
	(2) Glassblowing shop	600	-
	(3) Communications	200	-
	Total Direct Costs	$52,610	$ -
	Indirect Costs (60.80% of salaries and wages)	6,690	11,988
	Twenty-four Month Total	$59,300	$11,988

FIG. 2. The atom-probe budget.

evaporation, which actually allows the surface species to be determined.

The theory of field evaporation has been covered in detail elsewhere [4, 5], and, therefore, will not be reviewed here. Basically, it describes the field ionization of a surface atom or molecule followed by thermal activation over a field-reduced energy barrier. The result is that surface species, in the form of positive ions, may be removed

from the metallic emitter at a well-defined, controllable rate. The rate is fixed by the electric field strength at the surface and, therefore, by the potential difference applied between emitter and screen. Coupling this source of surface ions with a mass spectrometer, a suggestion first advanced by Müller [6] permits their mass-to-charge ratio to be determined. Because the field evaporation theory, even in its somewhat contrived form, can usually predict the charge of the evaporated species, the mass is also known.

Because of experimental difficulties in obtaining long-term ion currents of appreciable magnitude from a field evaporation source, most previous experiments have been concerned with field ionization—not evaporation-mass spectroscopy. This technique utilizes the extremely high electric field near the tip to ionize ambient gases or organic vapors, the ions formed being analyzed in a suitable spectrometer. Ingram and Gomer [7] presented the first experimental results with the publication of their study of the field ionization of hydrogen and deuterium.

Later, Müller and Bahadur [8] investigated, qualitatively, the field ion spectrum of hydrogen. Clements [9], studying the abundance of ion species in high ambient gas pressures, discovered the H_3^+ ion in the field ionized hydrogen spectrum. Beckey et al. [10] extended the technique to include the study of field induced dissociation products of hydrocarbons, using both conventional electron impact, and modified field ionization sources. Thomsen [11] in addition to studying the low-pressure spectra of field-ionized gases, reported the first observation of an abundant field evaporated ion, CuH_2^+, during his investigation of the field evaporation of beryllium copper in 10^{-7} Torr of hydrogen. Barofsky [12] originally continued Clements' study of the field-ionized hydrogen spectra, but later [13] was able to examine the low-temperature field-evaporation products of Be, Fe, Zn, and Cu. His investigation of the last metal confirmed Thomsen's original observation of the abundant CuH_2^+ ion.

Although Thomsen's work, and more particularly Barofsky's, resulted in the detection and identification of surface species during field evaporation, both investigators were limited by their apparatus. Thomsen did not have a suitable detector. Neither could localize the region of the emitter from which the ions originated, neither could preselect surface species of interest, and neither could work with fewer than perhaps 10^4 ions per second entering their spectrometers.

It is quite apparent that a major advance in both field ion mass spectroscopy and surface physics would be achieved with the positive identification of the atomic species associated with preselected, individual, image spots. To accomplish this feat, Müller [14] in 1967, realizing that single ion detection was possible, suggested a novel combination of field ion microscope and mass spectrometer now called the atom-probe FIM. The device, incorporating single-particle detection capability, relies upon the strict time correlation between a field evaporation and detection event to eliminate random detector noise.

The atom-probe was named (according to Riviere [15] incorrectly) in analogy with the well-known electron microprobe developed by Castaing [16]. This instrument, a combination electron microscope and X-ray analyzer, can investigate the constituents of a small section of specimen which, although typically of the order of 1 μm in size, still contains 10^{11} atoms. The scanning electron microprobe developed by Crewe [17], using a field emission source and an energy analyzer, may provide still another form of chemical analysis of selected specimen areas. The number of atoms involved, however, would still be greater than 10^5.

Only with the atom-probe FIM can one, ultimately, determine the identity of a single species seen with atomic resolution at a metal surface, and selected from neighboring atoms at the discretion of the experimenter. It is the purpose of this work to present, in some detail, the development of this most sensitive tool for microanalytical research.

THEORY OF OPERATION

The atom-probe consists of a field ion microscope modified so that the imaged atom chosen for analysis can be positioned over a small aperture, or "probe hole," in the microscope's phosphor-coated screen. This probe hole provides an entrance into the analyzer, which in the present designs has been a time-of-flight mass spectrometer with single-particle resolution. After properly positioning the specimen so that the desired surface atom is imaged over the probe hole, and pumping away the imaging gas if desired, the specimen is subjected to a high-voltage pulse. This pulse, superimposed on the steady-state DC imaging voltage, is made sufficiently large so that the resulting electric field at the surface will cause a number of surface atoms to field evaporate as positive ions. Only the atom that was imaged over the probe hole passes, now as an ion, into the time-of-flight mass spectrometer—all of the other ions being blocked by the screen.

After traveling approximately 1m, the ion collides with the first dynode of a multistage electron multiplier, thereby producing a signal that can be displayed on an oscilloscope. The recorded sweep, initiated by the evaporation pulse, is a direct measure of the ion's travel time. If the duration of the evaporation pulse is made longer than the ion's travel time in the acceleration region near the tip, the evaporated ion will quickly attain a kinetic energy determined solely by the sum of the DC imaging voltage and evaporation pulse voltage. That is:

$$1/2 \, m \, v_t^2 = ne(V_{dc} + V_{pulse}) \tag{1}$$

where ne is the ion's charge, and v_t its final, or terminal, velocity. Because the acceleration region near the tip is very short compared to the ion's total flight path, its travel time is, to a very good approximation, just

$$t \sim (d/v_t) \tag{2}$$

where d is the total tip to detector distance.

The ion selected for analysis is identified by its mass-to-charge ratio expressed as a function of the total voltage, travel time, and distance. Combining Eqs. (1) and (2) gives the desired result:

$$(m/n)_o = K(V_{dc} + V_{pulse})t^2 \tag{3}$$

where

$$K = 0.193/d^2$$

and V_{dc} and V_{pulse} are measured in kilovolts, t is measured in microseconds, and $(m/n)_o$ is expressed in terms of atomic mass units (amu). The constant K can be evaluated once the tip-to-screen distance, d, is known. For our instrument three different analyzer tube lengths have been used. Correspondingly, for $d = 0.82m$, $K = 0.228$; for $d = 0.99m$, $K = 0.195$; while for $d = 1.98m$, $K = 0.049$.

A PROTOTYPE INSTRUMENT

To demonstrate the feasibility of the atom-probe concept, a prototype instrument was constructed. Although it has been fully described elsewhere [18], its essential features will be repeated here, both for completeness and to provide a comparison with the improved instrument to be described shortly.

Figure 3 is a schematic diagram of the prototype atom-probe, while Fig. 4 is a photograph of the instrument itself. The specimen to be examined is spot welded to a molybdenum wire loop that is held in position by two tungsten coils. The coils are formed from tungsten wires that are sealed through the base of a Pyrex cold finger. These wires provide electrical contact to the specimen while cooling it by conduction from the cryogenic liquid through which they pass. A grounded aluminum cone, making thermal contact with the cold finger, surrounds the tip and its mounting coils. Such a cone has been shown by Müller [19] to increase the intensity of the faint FIM image by as much as 300%.

The entire cold finger is inserted into the upper portion of the microscope body with the specimen tip positioned as closely as possible to the center of rotation of the
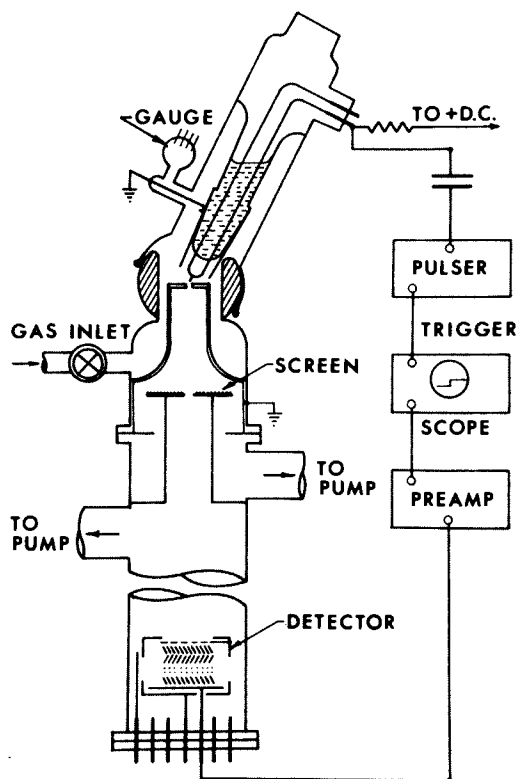
FIG. 3. The prototype atom-probe (schematic).

FIG. 4. The prototype atom-probe (photograph).

greased ball joint assembly. When so placed, the tip is axially aligned with respect to the holes located in both the aluminum plate and the fluorescent screen. The aluminum plate serves to separate the microscope into two sections. The upper, containing the tip, is connected to a supply of helium gas whose flow rate can be accurately adjusted. The lower portion, containing the screen, is connected to a liquid nitrogen trapped, 5cm, oil diffusion pump. During imaging of the specimen, the lower portion of the microscope body is pumped while helium gas is admitted into the upper portion. This dynamic gas supply system [20] allows operation with 1mt of imaging gas in the immediate vicinity of the tip, while maintaining the region near the screen at a considerably lower pressure.

The time-of-flight spectrometer, located directly behind the fluorescent screen, is continuously pumped by a separate, trapped, 5cm, oil diffusion pump. With a probe hole

1mm in diameter, the vacuum in this region is maintained, during imaging, at better than 5.0×10^{-6} Torr to ensure that an adequate mean free path is obtained.

The evaporation pulse is supplied by a Huggins Laboratory pulse generator, model 961D, which provides both adjustable pulse amplitude (0 to 3kV), and width. For the prototype atom probe a pulse width of 2.0 ns was chosen, with a corresponding rise and fall time of 0.5 ns. The actual pulse shape produced by the generator was observed at its output with a Tektronix type 519 oscilloscope. Manually triggered single pulses are normally used to field evaporate selected species, although the generator also permits 60-cycle repetitive operation. The evaporation pulse travels to the microscope head on a 50Ω coaxial cable terminated by a 50Ω resistor, and is coupled to the DC leads in the cold finger through a 500pF, 30kV capacitor.

A "venetian blind" electron multiplier having a gain of ~10^6 detects the field-evaporated species. The physical configuration of this detector [is similar to that of

the one used currently in the improved atom-probe, but *sic*] incorporates 12 Be-Cu dynodes, and one anode. The multiplier assembly, mounted on a brass O-ring flange, is bolted to the base of the time-of-flight tube; all electrical connections to the multiplier being made through ceramic-to metal seals soldered to the flange.

The anode of the electron multiplier is connected directly to a transistorized preamplifier originally designed by S. B. McLane [14] for a similar application. An overall current gain of greater than 10^{12} was observed with the detector preamp combination. The 16-ns rise time of the Tektronix type 551 oscilloscope, used to measure the time of flight, determined the rise time of the recorded pulse; the observed fall time of 1 ms was determined by the detector—preamplifier combination. Figure 5 is two typical oscilloscope photographs showing the recorded "staircase" wave shape resulting when two or more particles reached the detector during a single sweep. Because a single sweep lasts only 10 μs, and is initiated by the evaporation pulse, random events are effectively excluded from being recorded.

Preliminary results obtained with the prototype instrument indicated, at the relatively poor vacuum conditions present, the occurrence of tungsten–oxygen and tungsten–nitrogen compound ions on the surface. Figure 5(B) shows typical oscilloscope flight-time data obtained for a tungsten specimen. For the upper trace, the species is $^{182}W\ ^{16}O_2^{3+}$ ($m/n = 71$), while for the lower trace (from left to right), the species are $^{184}W\ ^{16}O_2^{4+}$ ($m/n = 53.6$), and $^{182}W\ ^{16}O_2^{3+}$ ($m/n = 71.2$). In addition, the evaporation of rhenium–molybdenum alloys indicated that both metals field evaporated as doubly charged ions. A similar result was obtained for tungsten specimens, but W^{3+} and W^{4+} were also observed. Figure 5(A) resulted from an examination of tungsten at 21K. A getter, installed near the tip, improved the background vacuum. For the upper trace (from left to right) $m/n = 66$ and $m/n = 91$. For the lower trace $m/n = 66$. These species are to be identified with $^{182}W\ ^{16}O^{3+}$ ($m/n = 91$), and $^{182}W\ ^{16}O^{3+}$ ($m/n = 66$) or $^{182}W\ ^{14}N^{3+}$ ($m/n = 66$).
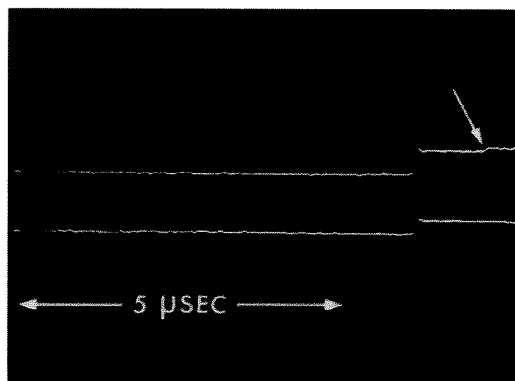
A. Tungsten at 9.0 kV + 0.2 kV pulse
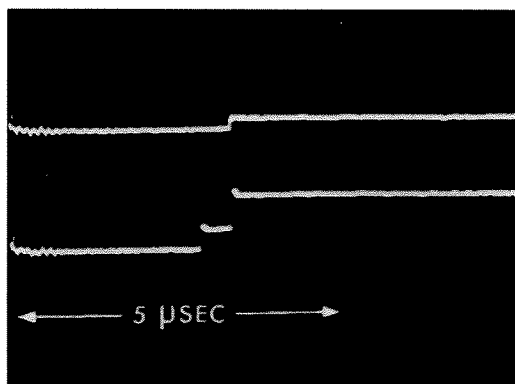
B. Tungsten at 25 kV + 2.4 kV pulse

FIG. 5. Atom-probe examination of tungsten.

Although a mass determination accurate to ±1.0amu was claimed, more refined experiments with the most recent instrument indicate that such a figure was probably quite optimistic. In fact, [as will be discussed shortly, *sic*] the very equation, Eq. (1), used for all the mass determinations, must be refined by the incorporation of two correction factors.

Another problem with the device was that, although any region of the specimen could be positioned over the probe hole, the poor viewing conditions prevented both precise selection of single species and photographing the image. Nevertheless, the prototype atom probe did demonstrate that the original concept of mass analyzing a single field-evaporated particle was feasible. In addition, it provided novel preliminary results by establishing the unexpect-

edly high ionic charges of some field-evaporated ions, while at the same time providing a firm basis on which to design future instruments.

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