(12)

CHARLES EVANS & ASSOCIATES

SPECIALISTS IN MATERIALS CHARACTERIZATION

December 19, 1985

Mr. Sven A. Roosild
Defense Advanced Projects Agency
1400 Wilson Blvd.
Arlington, VA 22209

Subject: Technical Progress Report
Contract No. N00014-85-C0858

Dear Mr. Roosild:

Enclosed please find the Technical Progress Report for our Contract entitled "The Development of Sputtered Neutral Mass Spectrometry for Quantitative Depth Profiling of Compound Semiconductor Materials."

Attached is a DD Form 250. Copies of the Report have been sent to the Administrative Contracting Officer, the Director of Naval Research Laboratory and to the Defense Technical Information Center as is specified in the contract.

Sincerely,

Dave Reed

David A. Reed
Project Manager

jg

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Technical Progress Report

from

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The Development of Sputtered Neutral Mass Spectrometry for the Quantitative Depth Profiling of Compound Semiconductor Materials

Sponsored by

Defense Advanced Research Projects Agency (DoD)

ARPA Order #4941

Under Contract #N00014-85-C-0858 issued by
Office of Naval Research, Department of the Navy
800 N. Quincy Street, Arlington, Virginia 22217-5000

Prepared for:

Defense Advanced Projects Agency
1400 Wilson Blvd., Arlington, Virginia 22209
Attn: S.A. Roosild

Principal Investigator:

Dr. David A. Reed

Effective Date: September 16, 1985

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Reporting Period: November 1 - December 15, 1985

Introduction

In the first contract progress report dated 5 November 1985, the sputtered neutral mass spectrometry (SNMS) data were obtained using a laboratory-built instrument at Kaiserslautern University, West Germany under the direction of Professor H. Oechsner as originally proposed. This instrument has been operational for a number of years and has been utilized by Professor Oechsner, his students and collaborators for many pioneering studies fundamental to the development of the technique. Recently, Leybold-Heraeus GmbH (LH) of Cologne West Germany has undertaken a program to commercialize SNMS instrumentation (the model INA-3 secondary neutrals mass spectrometer) in concert with professor Oechsner's research group. CHARLES EVANS & ASSOCIATES (CE&A) has entered into an agreement with LH to evaluate the applications potential of SNMS as implemented in the INA-3 for advanced materials characterization. This report will detail our initial hands-on experiences with SNMS via the LH prototype version of the INA-3 on loan to our laboratory. The availability of this instrument has dramatically increased our access to the technique thereby expediting this Phase I research program.

Hardware Considerations

The INA-3 is designed along the same lines as the Kaiserslautern instrument that was shown schematically in Figure 1 of the first progress report. The key functional components and parameters are:

1. The rf plasma uniquely established by pressure, rf power and external DC magnetic field,

2. Ion extraction optics consisting of an extraction electrode, focusing lens, 30° electrostatic analyzer (ESA) and transfer elements required to transport the energy filtered ion beam into a quadrupole mass spectrometer,

3. A conventional quadrupole mass filter with electron multiplier detector, and

4. The target bias supply.

In the latter case, the Kaiserslautern instrument references the target potential to the plasma potential via a Langmuir probe, whereas the INA-3 presently references the target power supply to ground potential (i.e., no

Langmuir probe). Our studies to date have indicated that a Langmuir reference might make a significant improvement. Within the past several weeks discussions have been held with LH senior technical staff regarding the need for plasma potential sample referencing for improved day-to-day reproducibility and to serve as a general purpose plasma diagnostic device. We have recommended incorporation of a suitable probe (Langmuir or other) on a spare flange on the INA-3 plasma chamber. This can be accomplished on a retrofit basis but will probably not be completed before the end of this Phase I effort. Although we cannot assess the exact impact this addition will have on instrument performance and data reproducibility, our expectation is that the improvement will be substantial.

Quantitation and Detection Limits

Figure 1 shows a quasi-conventional positive ion SIMS spectrum taken from bulk GaAs using the INA-3 with 5 KeV Ar^+ ion bombardment. The INA-3 can be operated as a conventional quadrupole SIMS instrument with an auxiliary ion gun for sputtering and with the plasma off, although it is dramatically less capable than a standard Cameca IMS-3f SIMS. We refer to Figure 1 as "quasi-conventional" because the plasma chamber contained Ar gas at the pressure normally used in SNMS operation. The plasma, however, was off.

The Ga^+ to As^+ ratio calculated from the integrated peak intensities of Figure 1 is approximately 7000 manifesting the typical SIMS ionization potential (IP) dependence of the ion yield which often complicates conventional SIMS quantitation and degrades detection limits for the high IP elements when using positive secondary ion mass spectrometry. A similar ratio is observed when using O_2^+ primary beams with a Cameca IMS-3f. Figure 1 also reveals the presence of several relatively intense molecular ion species (e.g., GaO^+ and $GaOH^+$) which also tend to generically complicate SIMS analysis, especially when using a quadrupole mass spectrometer based instrument. Most of the remaining mass peaks observed arise from neutral beam sputtering of the sample holder. This issue is not relevant to conventional SNMS in the direct bombardment mode (DBM), but is a very serious problem for the so-called separate bombardment mode (SBM) of operation useful for the analysis of insulators. We have advised LH of the problem and suggested additional differential pumping along the ion beam path, modified ion beam optics, a redesign of the sample holder or some combination thereof to reduce this effect.

Figure 2 shows an SNMS spectrum taken from the same GaAs sample and vividly illustrates the distinction between the two techniques (SIMS and SNMS). Although we can clearly see that SIMS appears more sensitive in terms of absolute Ga intensity and As intensity, SNMS provides a much more uniform ionization yield, virtually independent of IP. (Ga and As differ in IP by about 4eV.) Furthermore, we do not observe any significant evidence for molecular ions in the SNMS spectrum. Either sputtered neutral molecules are not ionized in the plasma or they are dissociated into atomic ion and neutral fragments by collisions with plasma gas molecules.

What we do find unique to SNMS is a contribution from plasma gases (dominated by $^{40}Ar^+$ in this case) which come about partly by direct extraction of plasma gas ions and partly from sputtered secondary neutral plasma gas species previously incorporated into the sample during sputter etching (i.e., ion implantation). Plasma gas ions can be mostly excluded from the spectrum by very careful tuning of the extraction ion optics. This effect takes advantage of the differences in the energy distributions of true sputtered neutrals and plasma gas ions. Contributions due to implanted plasma ions are unavoidable.

A second significant feature seen in Figure 2 is the rather noisy but continuous background on which the individual mass peaks are superimposed. This background is also observed by LH and Professor Oechsner in their respective instruments. The present theory is that the background arises from stray UV light and/or spurious photoelectrons associated with the plasma ions arriving at or produced in the vicinity of the electron multiplier. Our experiments, duplicated by LH, indicate that the magnitude of the background can be strongly influenced by the exact tuning of the ion optics. In Figure 2 the peak count rate for $^{69}Ga^+$ is about 8000 cps while the background is nominally 50 cps giving a peak-to-background of 160. However, as shown in Figure 3, by modifying the tuning of the optics we can achieve more absolute signal (195,000 cps peak count rate for $^{69}Ga^+$) and a peak-to-background of about 2000 at the expense of a slightly higher absolute background level (100 cps) and a greater contribution from the plasma gas. There seems to be a complex relationship between background, plasma gas ions and plasma temperature (reflected in the Ga^+/As^+ ratio) which we are currently investigating. We have discussed the matter with LH personnel who are endeavoring to modify the optics so as to eliminate or at least substantially reduce the continuum background. Moreover, studies are currently in progress under the auspices of this contract to better characterize the Ga^+/As^+ ion intensity ratio (critical for quantitation) which will be included in the next

progress report. The background signals, plasma gas ions and total achievable matrix ion intensities are currently dominating detection limits while the factors giving rise to variabilities in the Ga^+/As^+ ratio will ultimately limit measurement accuracy.

High Resolution Depth Profiling

As was seen in the depth profiles taken at Professor Oechsner's laboratory and presented in the first progress report, SNMS offers the promise of very high depth resolution (<<100 angstroms) profiling of multilayer structures, thin films and interfaces with improved quantitation. Early attempts to duplicate the results obtained in Germany using the INA-3 in our laboratory were unsuccessful for reasons that remain unclear. Initial attempts to depth profile the microscopically modulated thin films met with some difficulties since there are at least five interdependent variables, viz. pressure, RF power, external magnetic field, target bias and sample/plasma aperture distance that influence the uniformity of the sputter etching front which in turn governs depth resolution. In addition, once we established the appropriate operating conditions it was determined that sample introduction and profiling protocols also play an important role in achieving high quality depth profiles. Most notable is the fact that a minimum wait of twenty minutes or more is necessary for the plasma to "stabilize" after a sample is introduced into the plasma chamber. (Samples may only be analyzed once per loading with the present sample introduction system.) Having overcome these difficulties, a number of "high resolution" depth profiles have been obtained using the INA-3 in our laboratory as shown in Figures 4 through 8. The range of modulation repeat distance represented by these samples is about 40 to 120 angstroms (approximately 20 to 60 angstroms individual layer thicknesses assuming the dissimilar layers to be equally thick). Quotation marks have been used around the term high resolution above because we are not yet sure just what depth resolution means in the context of these modulated thin film samples and the structure of the SNMS sputtering crater. With the very low energy ion bombardment we have overcome the limitations to depth resolution due to ion beam mixing and now are confronted with crater geometry issues alone.

A typical SNMS crater is circular with a diameter generally less than or equal to the plasma aperture diameter (5mm in the INA-3). There are two geometrical factors that limit depth resolution: 1) flatness over the entire crater bottom (related to the uniformity of current density during sputtering) and 2) crater

edge contributions. Our experience thus far has suggested that for these modulated composition films, nonuniform crater bottoms give rise to various "beating" type structures, whereas a sloping crater edge produces a graded interface and a long tail on the profile beyond the interface appearing as a large Ta "background" in the substrate region for these particular samples. The latter effect can be seen in all of the profiles shown herein. At the beginning of each profile a number of data channels were acquired with no target bias in order to establish plasma background at mass 181 amu. Experiments are in progress to find a practical solution to the crater edge rejection problem and to attempt to deconvolve crater edge effects from non-uniform crater bottom effects insofar as they individually limit depth resolution.

Even though the profiles are manifesting crater shape artifacts in some form or fashion, we are able to discern detailed sub-structure in the samples, particularly around substrate interfaces. Figure 8 is the most pronounced in this regard where it would appear that an extra thick layer was initially deposited as if the deposition shutter was opened prior to rotating the platen. Not knowing the detailed mechanics of the deposition system or the exact deposition history of the specimen we can only speculate, but the extraordinary thickness of the first deposited metal layer may be nothing more than an inertial effect. More peculiar is the profile shown in Figure 6. Here it is one of the intermediate layers that exhibits a nonregularity as if perhaps the Si source failed to function or functioned improperly during one half deposition cycle. Additional sub-structure can be seen in the ensuing layers as the interface is approached. More investigations will be required on this particular specimen in order to deduce the true compositional structure. Once that is accomplished we may be able to gain more confidence in our ability to accurately interpret any given SNMS profiling result.

Reproducibility of the depth profiles illustrated in the previous several figures has been, at best, elusive. Each of the profiles shown is one of numerous attempts of each sample taken under very careful systematically varied experimental conditions while searching for the optimum response. Once an optimum set of conditions was found on a given day several samples could be analyzed consecutively with reasonably good depth resolution. In one such series, however, a sample was analyzed four separate times with inferior results. Figure 9 shows one of the profiles obtained during that experiment. When a different sample was analyzed afterwards, it gave as good a result as had been obtained two hours earlier. It would appear that the particular

sample shown in Figure 9 exhibits an unusual behavior, although admittedly the modulation repeat distance is less than 40 angstroms. Depth profile reproducibility and day-to-day variability questions are serious matters presently under investigation that will be further examined in a subsequent progress report.

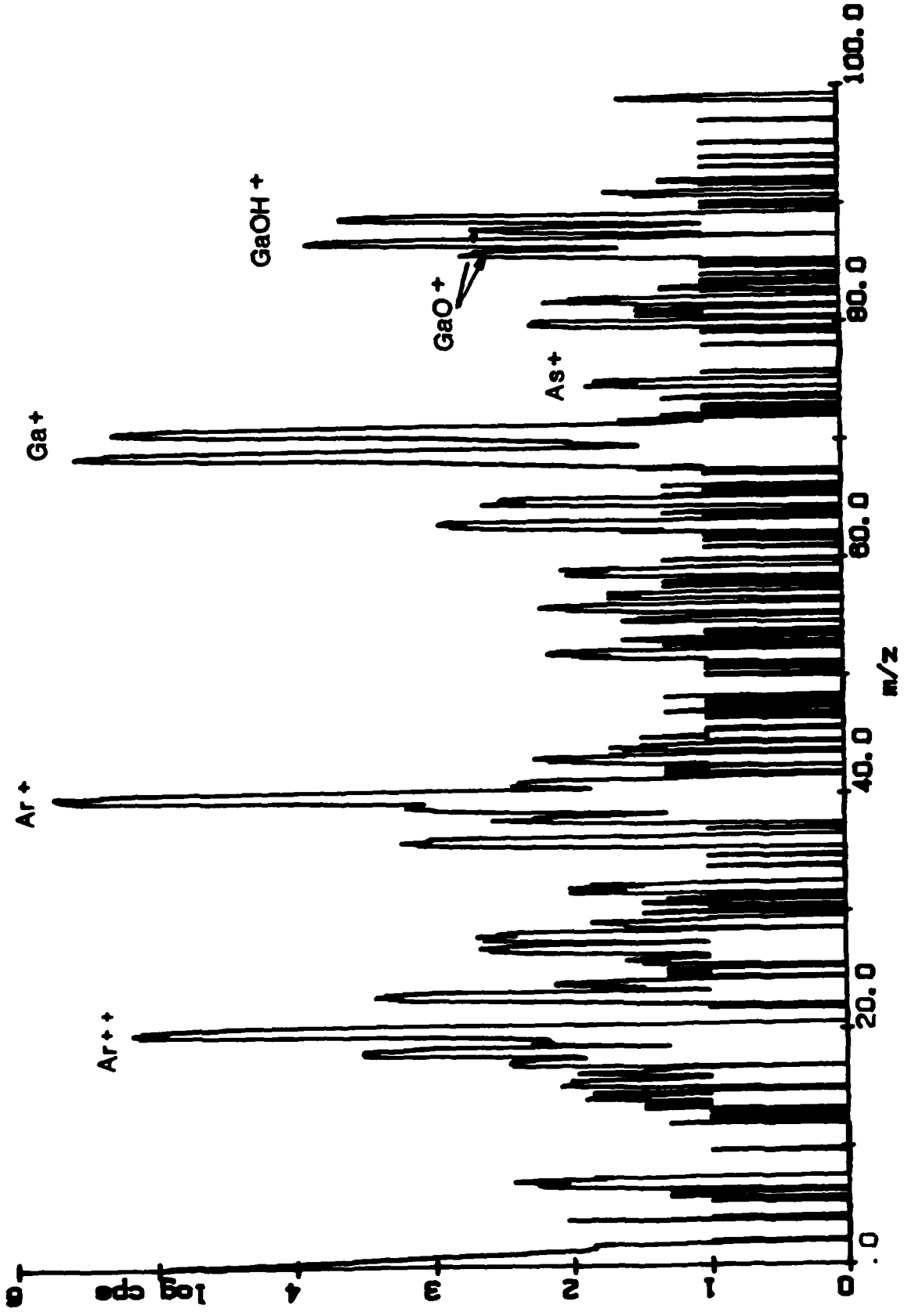

Figure 1

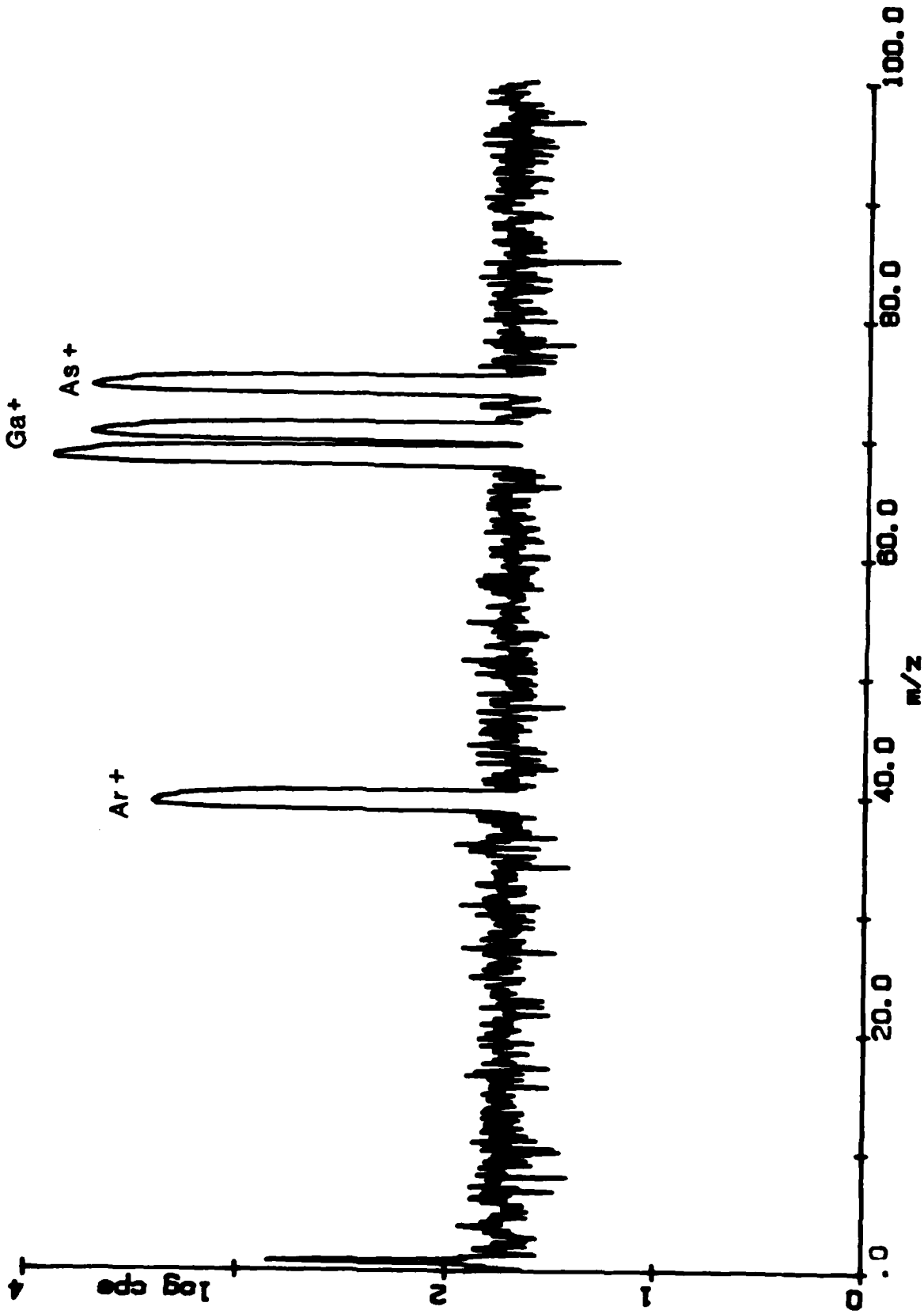

Figure 2

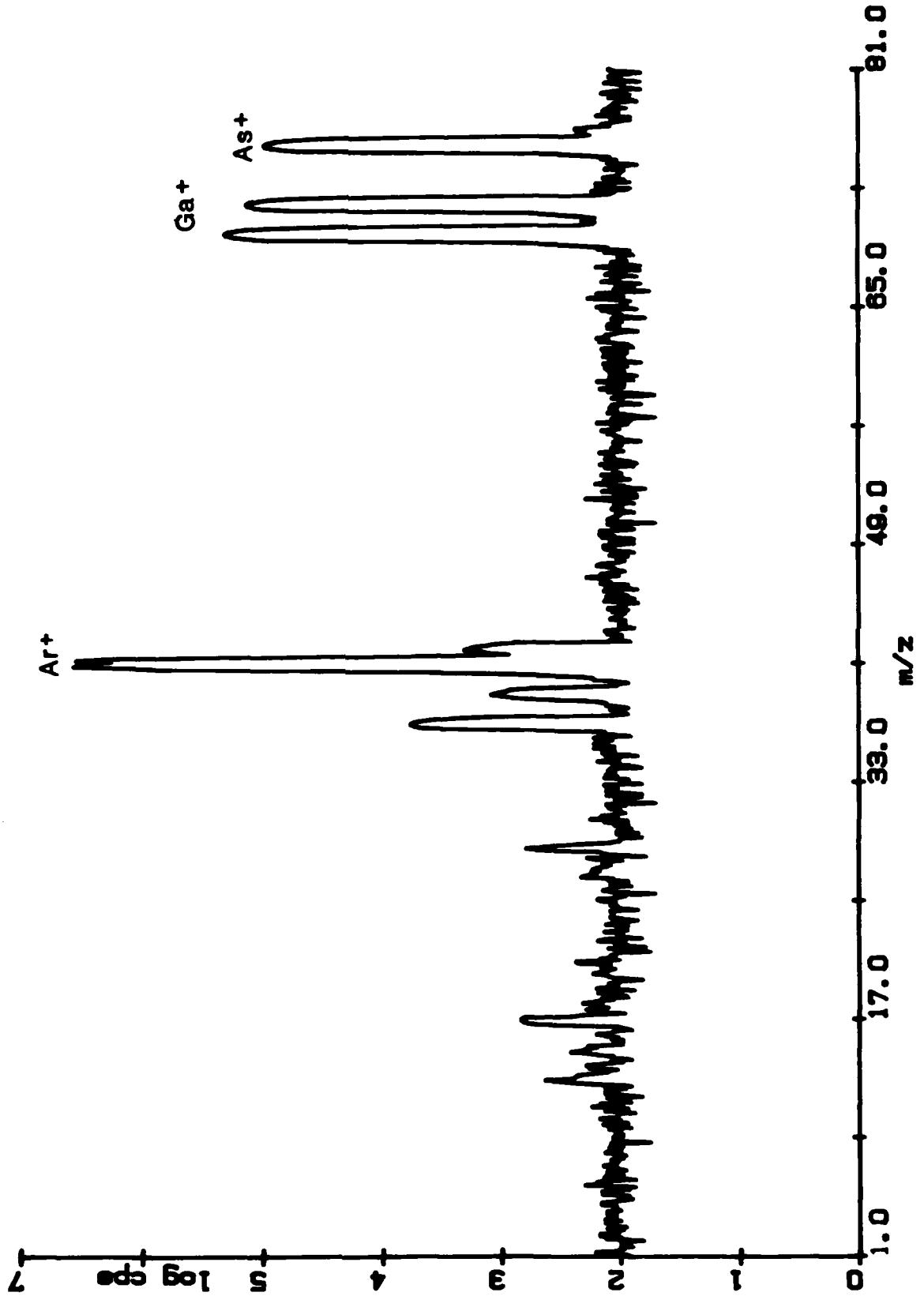

Figure 3

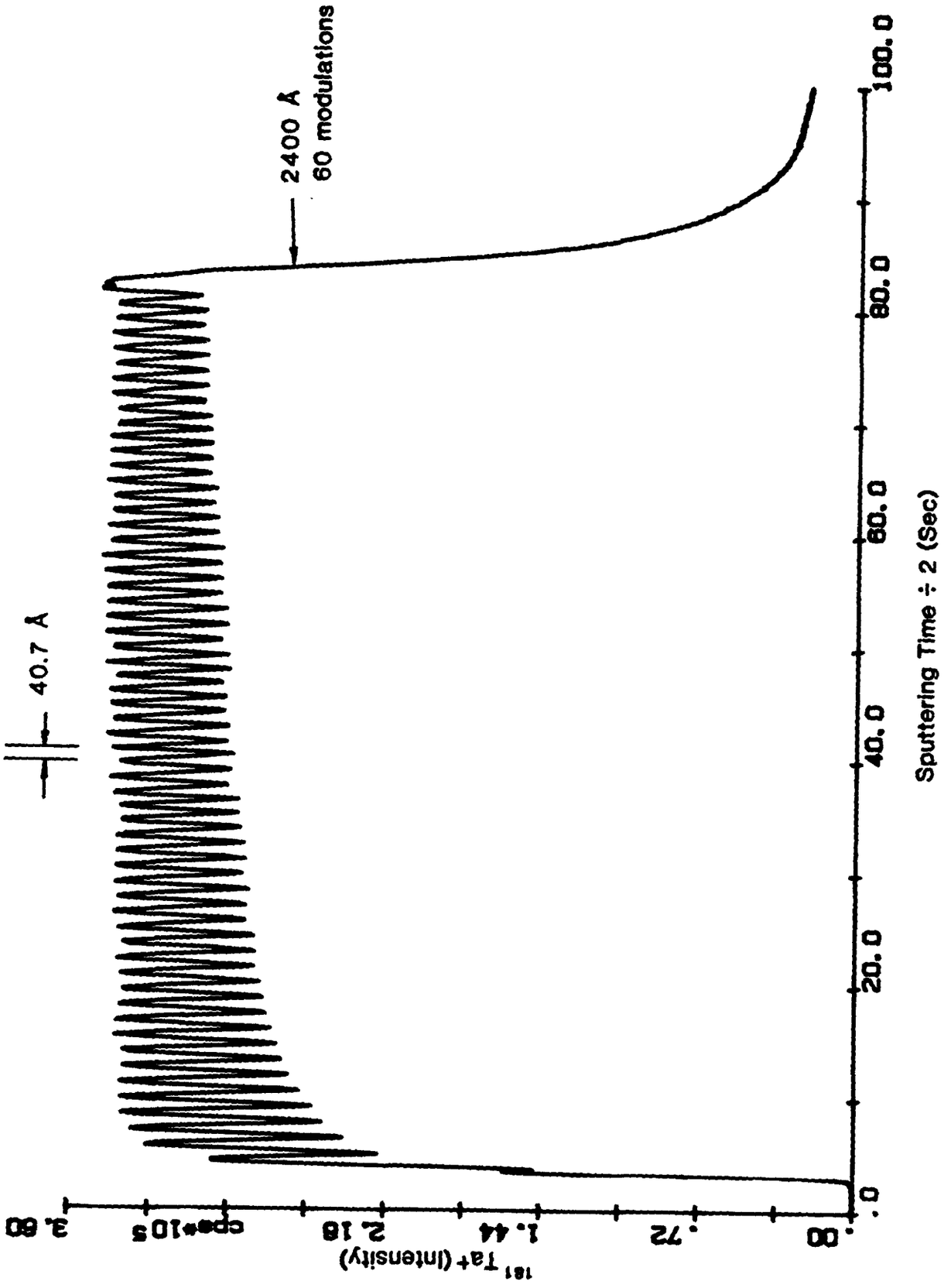
2400 Å
60 modulations
40.7 Å
0.
20.0
40.0
60.0
80.0
100.0
Sputtering Time ÷ 2 (Sec)
.08
.72
1.44
2.18
cps*10⁵
3.80
181 Ta+ (Intensity)

Figure 4

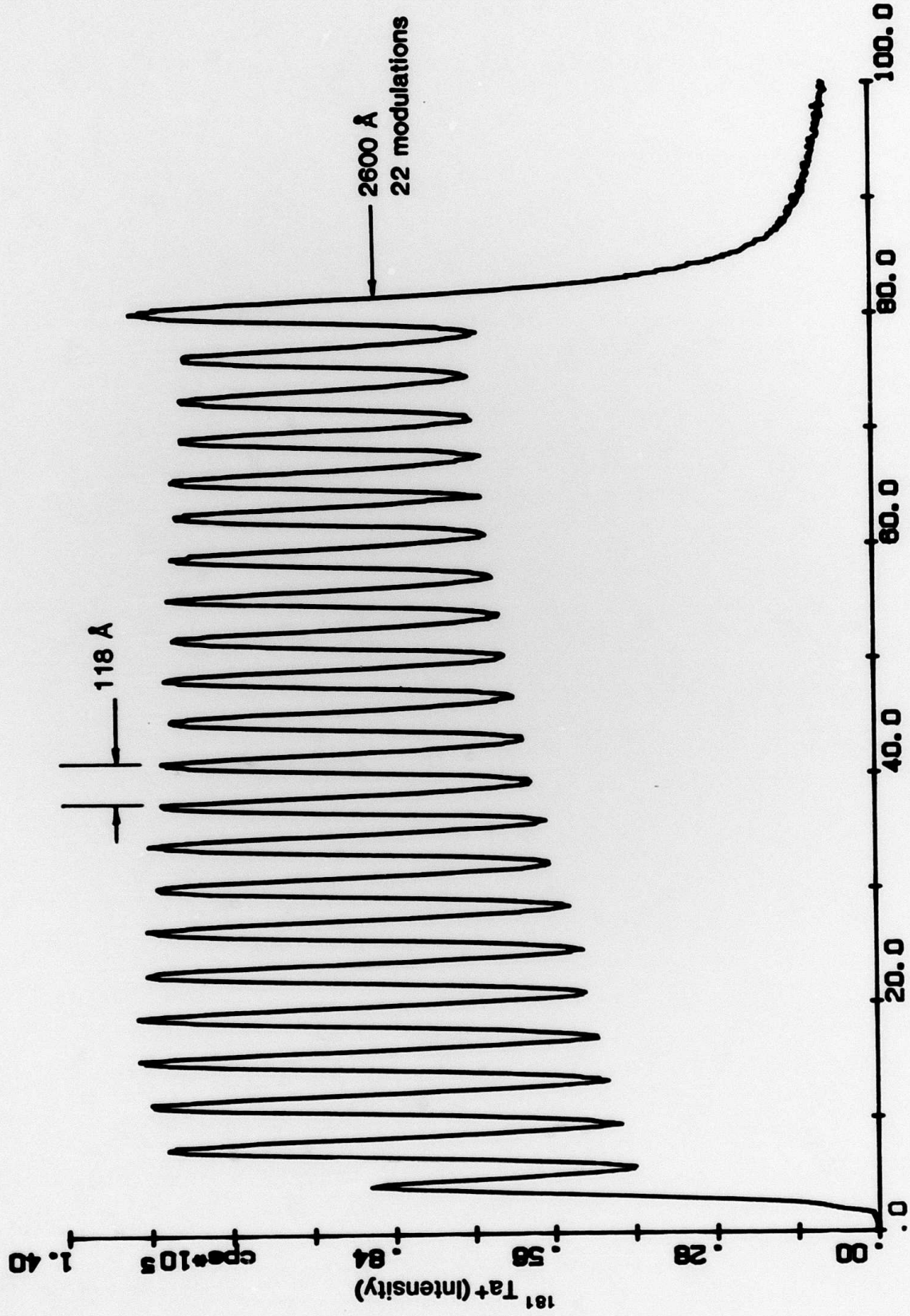
2600 Å
22 modulations
118 Å
$^{181}Ta^{+}$ (Intensity)
cps*10^{5}
1.40
.84
.56
.28
.00
0.
20.0
40.0
60.0
80.0
100.0
Sputtering Time ÷ 2 (Sec)

Figure 5

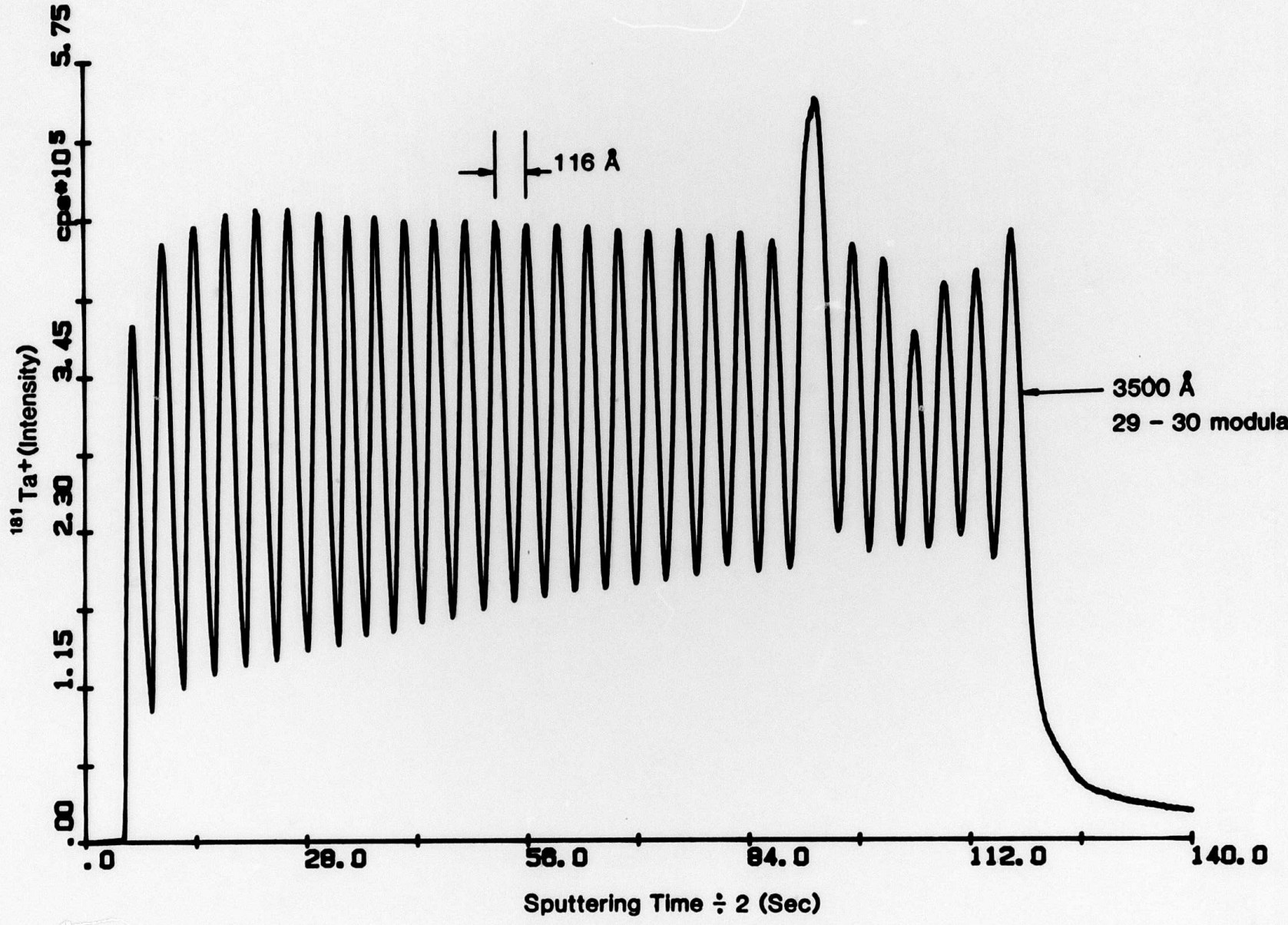
116 Å
3500 Å
29 – 30 modulations
$^{181}Ta^{+}$(Intensity)
.00
1.15
2.30
3.45
cps*10^{3}
5.75
.0
28.0
56.0
84.0
112.0
140.0
Sputtering Time ÷ 2 (Sec)

Figure 6

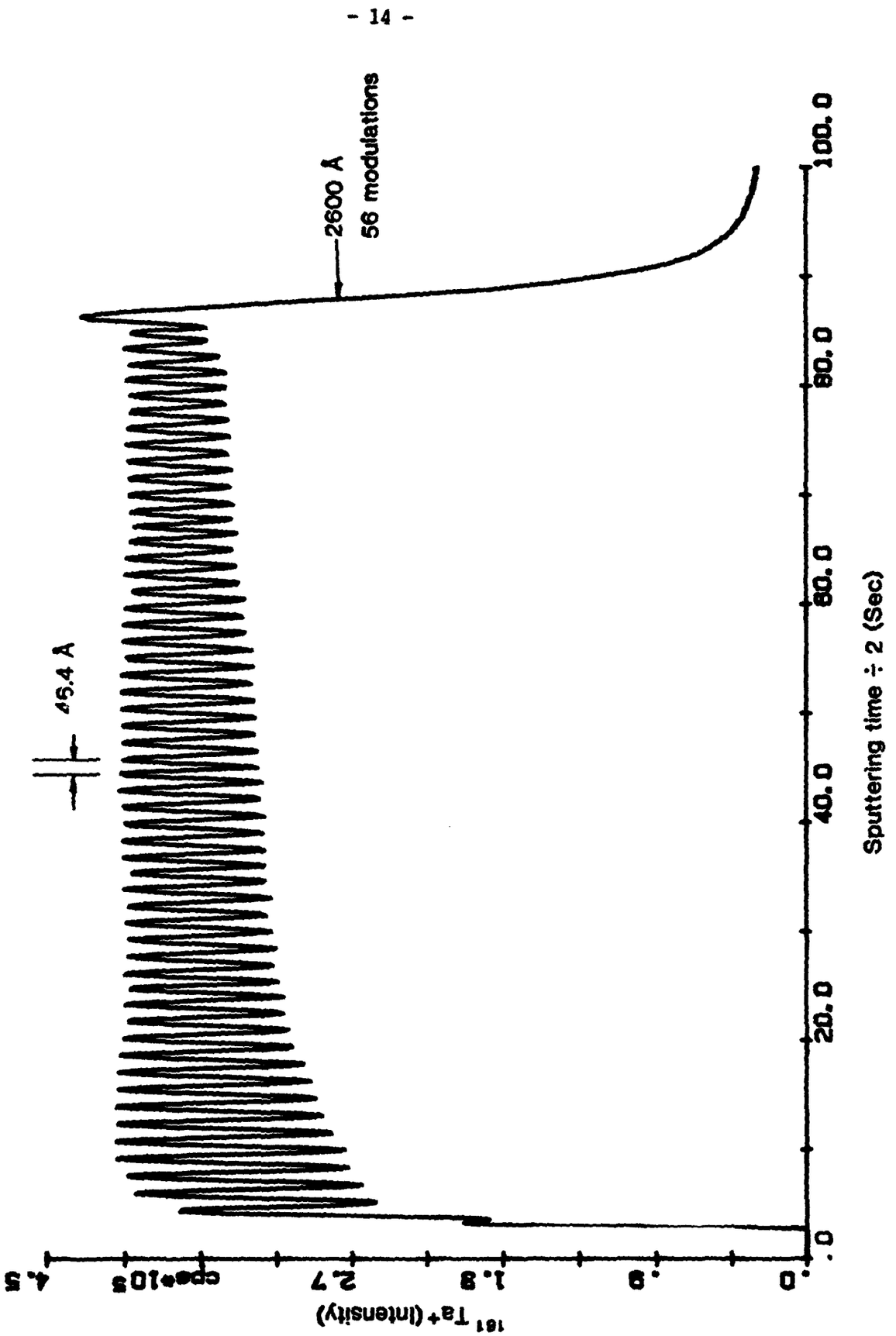
2600 Å
56 modulations
46.4 Å
181 Ta+ (Intensity)
0.
.9
1.8
2.7
cps•10³
4.5
0.
20.0
40.0
60.0
80.0
100.0
Sputtering time ÷ 2 (Sec)

Figure 7

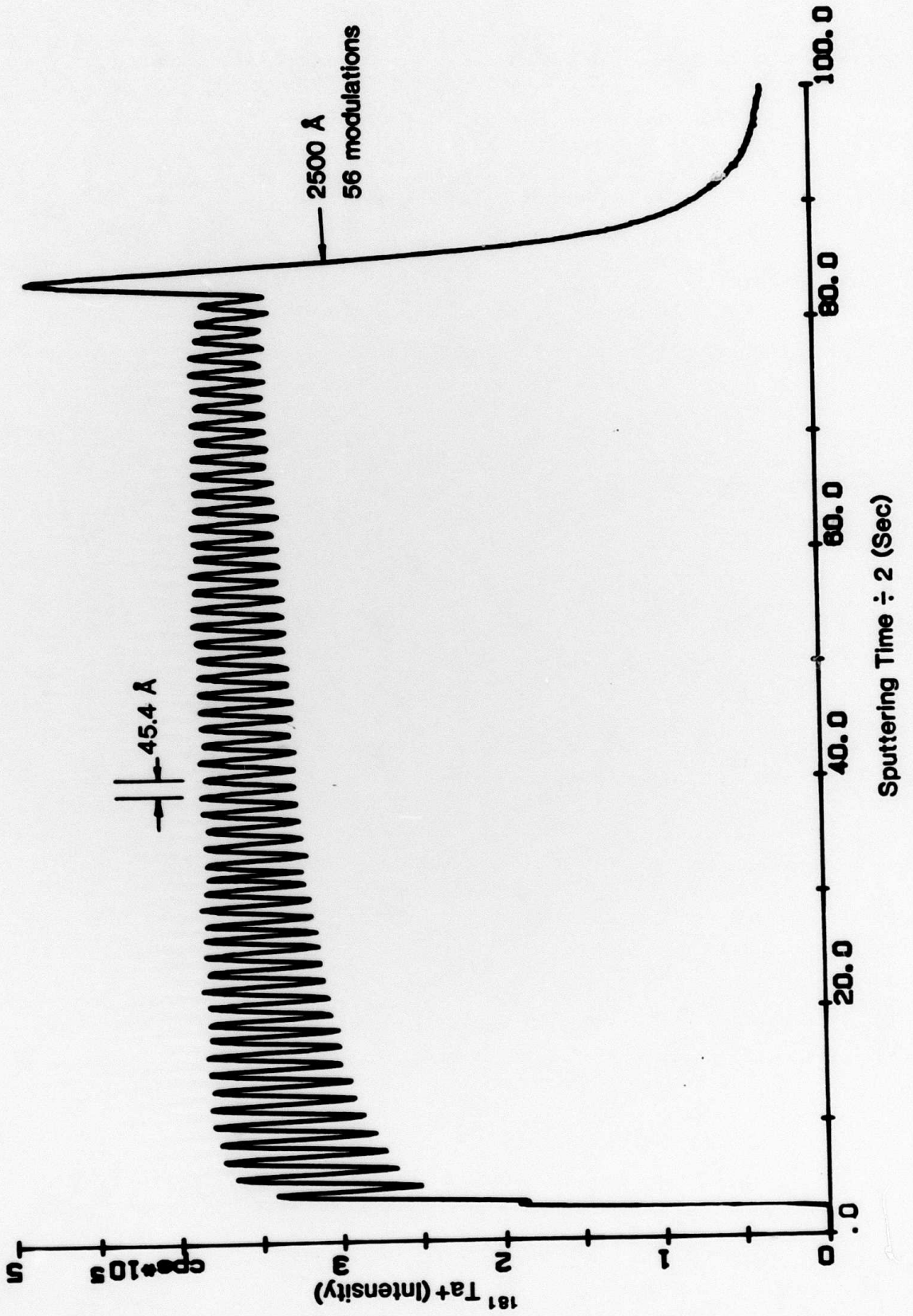
$^{181}Ta^{+}$ (Intensity)
cps*10^{5}
5
3
2
1
0
0.
20.0
40.0
60.0
80.0
100.0
Sputtering Time ÷ 2 (Sec)
45.4 Å
2500 Å
56 modulations

Figure 8

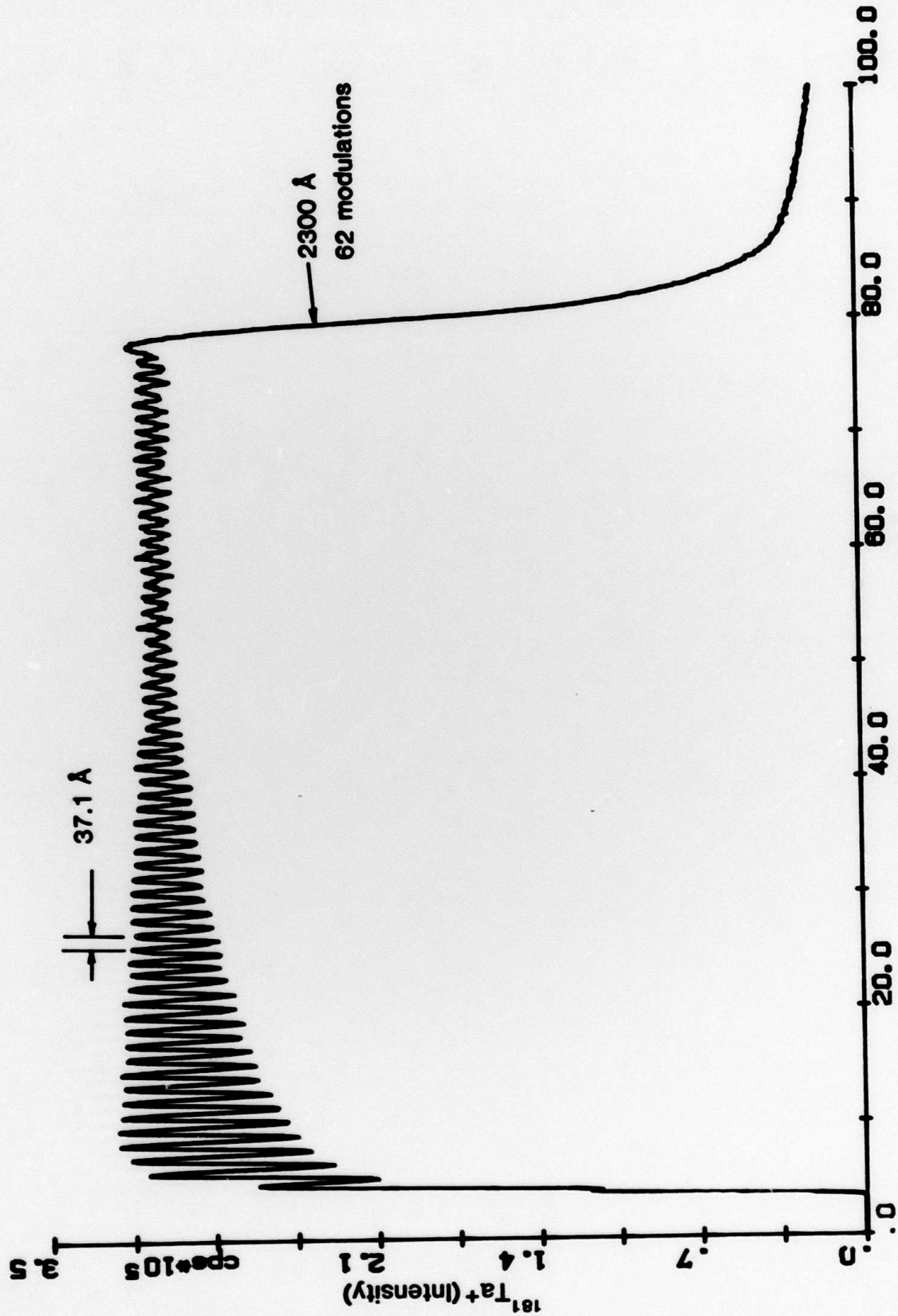
37.1 Å
2300 Å
62 modulations
$^{181}Ta^{+}$ (Intensity)
cps*10^{5}
3.5
2.1
1.4
.7
0.
0.0
20.0
40.0
60.0
80.0
100.0
Sputtering Time ÷ 2 (Sec)

Figure 9