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CONTACT RESISTANCE AND ADHESION CHARACTERISTICS OF OXIDIZED TANTALUM NITRIDE MIRRORS

D. K. Kramer

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November 1975

ABSTRACT

Oxidation of tantalum nitride resistor films used in hybrid microcircuits is an unavoidable phenomena known to affect interfacial properties between resistor and conductor layers. At room temperature, oxide thickness increases with time at an unknown rate; therefore, a three-day limitation between Ta_2N and Cr/Au conductor deposition is presently specified for hybrid microcircuits.

The effects of Ta_2N aging on resistor-conductor contact resistance and conductor bondability were evaluated. Accelerated aging produced oxide layers of various thicknesses which were then correlated to contact resistance. Analytical data and calculations indicate that a 25% increase in contact resistance would occur by exposing the Ta_2N to air for approximately three years at room temperature and pressure prior to metallization. However, little or no change in bondability would be expected.

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INTRODUCTION

Chromium-gold conductor metallization and tantalum nitride thin film resistors are presently utilized in the Sandia hybrid microcircuit technology. Preceding the conductor metallization, 500 Å of tantalum nitride (Ta_2N)[1] are reactively sputtered onto alumina substrates to provide 100 ohms/square resistors in the completed circuits. The substrates are then cooled to approximately 100°C in vacuum before exposure to air. They are then removed from the vacuum system and stored in a clean air environment until the Cr/Au conductor metallization is evaporated onto the mirrors.

The surface of the Ta_2N film will oxidize when exposed to air with the thickness of the oxide depending upon time of exposure and the temperature. Organic contaminants can also form on the oxide.[2] Previous publications have noted that minimizing the thickness of these contaminants will facilitate adhesion of the chromium film.[2] D. A. McLean also suggested that increased storage time would lead to increased contact resistance.[4] Therefore, the Cr/Au deposition specification for HMC's requires that the Cr/Au deposition be performed within three days after the Ta_2N deposition.[2,3] However, the high capacity of the new continuous Ta_2N sputtering facility at BKC has led to a desire to stockpile the Ta_2N mirrors for a longer time prior to Cr/Au deposition.

The purpose of this study was to experimentally determine the effect of a Ta_2N oxide layer on the resistor-conductor interfacial properties. The quality of the resistor-conductor interface adhesion as well as electrical contact resistance may be closely related to oxide thickness and surface contamination.

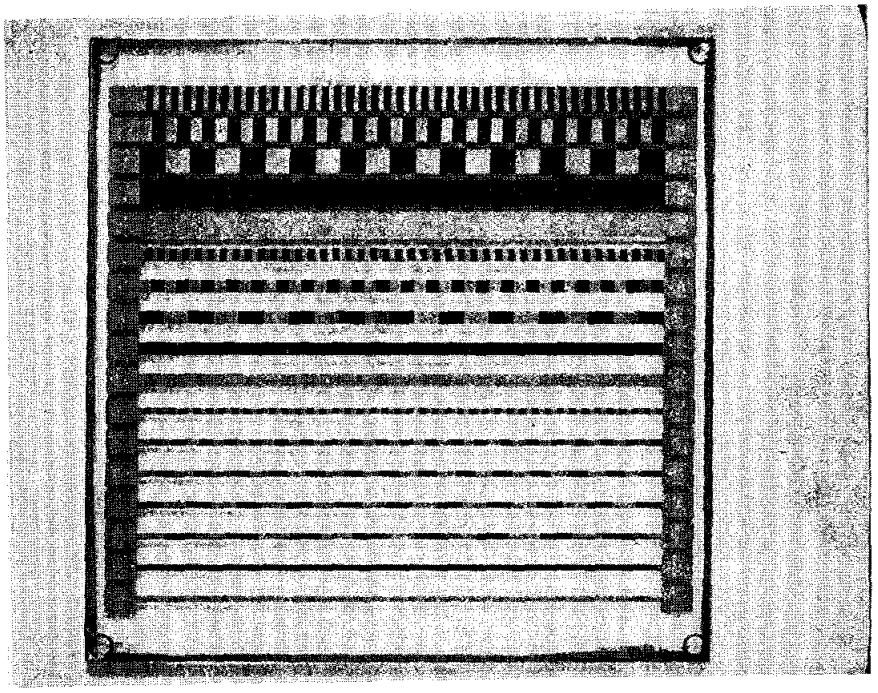
EXPERIMENTAL PROCEDURES

Sample Preparation

Since the interfacial or contact resistance between Ta_2N and Cr/Au is small compared to the resistance of the Ta_2N resistor, a resistor test pattern with a large number of interfacial contacts in series was required.[6] Therefore, a test pattern was designed to evaluate the change in the resistance of metallization-tantalum nitride contacts as a function of aging time. The pattern used consisted of a series of resistors terminated at both ends with Au bonding pads (Figure 1). Line widths of 10, 20, and 40 mils with alternating conductor and resistor pads of 10, 20, 40, and 50 mil lengths were incorporated in the design. Continuous patterns of Ta_2N and conductor coated Ta_2N were included on the same substrate to evaluate the sheet resistivity of the individual materials. Eleven intermittent resistors, three Ta_2N, and three conductor lines were accommodated on a 25.4 mm x 25.4 mm sapphire substrate. The intermittent pattern causes the current to cross the resistor/conductor interface up to 84 times, hence, any change in contact resistance produces a measurable change in total resistance.

Sandia HMC procedures and specifications were followed in Ta_2N deposition, Cr/Au deposition, and photolithography. DC diode reactive sputtering of tantalum in a nitrogen-argon mixture produced a film composition of approximately Ta_2N.[1] Approximately 500 Å of Ta_2N was sputtered in a Consolidated Vacuum Corporation oil diffusion pumped system using the parameters shown in TABLE I.

Prior to metallization, the resistor films were oxidized by heating at 300°C in atmospheric air for controlled time periods. Thermal oxidation time varied from 0 to 4 hours in half hour time increments for a series of 18 substrates (2 substrates for each bake time). This procedure was designed to yield oxide layers of various



Contact Resistance Test Pattern

Figure 1

TABLE I

substrate temperature	400°C
nitrogen flow	6.2 to 6.4 standard cubic centimeters per minute
pressure	2.13 to 2.39 Pa
sputter voltage	5 kV
sputter current	180 mA

thicknesses. A 300 Å chromium adhesive layer and a 30,000 Å gold conductor layer were then deposited by vacuum evaporation in an NRC Equipment Corporation oil diffusion pumped system using the parameters shown in Table II. The deposition was done from tungsten boats resistively heated.

TABLE II

substrate temperature	350°C
pressure	2.66×10^{-4} Pa.
Cr deposition rate	250 Å per minute
Au deposition rate	2000 Å per minute

Both alumina and sapphire substrates were considered for this study. However, alumina was eliminated because of the inconsistency and scatter of the contact resistance data due to surface roughness. All the data presented in this report were obtained using sapphire substrates.

50.8 mm square high resolution glass masks, Shipley 1350 J positive photoresist filtered to 1 micron, and a Preco exposure console were used for photolithographic definition of the previously described pattern onto the metallized substrates. The etchants that were used are shown in Table III.

TABLE III

Gold etch	- Potassium Iodide + Iodine 220 gm. Potassium Iodide 127 gm. Iodine DI water to make 1 liter
Chromium etch	- Cerric Ammonium Nitrate 164.5 gm. Cerric Ammonium Nitrate 90 ml Nitric Acid DI water to make 1 liter
Tantalum Nitride etch	- Hydrofluoric and Nitric Acid Solution 40 ml Nitric Acid 40 ml Hydrofluoric Acid 80 ml DI water

Analysis

The thermal oxide thickness was estimated by Auger electron spectroscopy (AES) in conjunction with in situ argon sputtering using a Physical Electronics Cylindrical-Mirror Auger Electron System. AES parameters are shown in Table IV.

TABLE IV

Analytical Parameters	
Primary voltage	5 KV
Primary current	10 μA
Modulation voltage	6 Vpp
Multiplier voltage	1900 V
Lock-In Sensitivity	200 μV
RC Time constant	0.3 sec.
Sputtering Parameters	
Voltage	1 KV
Current	5 MA
Pressure	6.65×10^{-3} Pa Argon

The sputter rate was estimated to be 7 Å per minute.[5] However, the system used in this study was not calibrated and, therefore, this number cannot be considered

absolute.

A more accurate determination of the oxide thickness was obtained by using multiple angle-of-incidence ellipsometry performed by J. R. Adams. Values for the oxide thickness were also calculated from sheet resistivity measurements on the tantalum nitride (assuming the resistivity of Ta_2O_5 is infinite) which were made before and after thermal oxidation using the derived formula

$$\frac{d_{oxide}}{d_{Ta_2N}} = \frac{\Delta R}{R} \quad \frac{\Gamma_{Ta_2N}}{\Gamma_{Ta_2O_5}} \tag{1}$$

where

d_{oxide} = thickness of oxide

d_{Ta_2N} = thickness of Ta_2N film (500Å)

Γ_{Ta_2N} = density of Ta_2N (16.3 gm/cm^3)

$\Gamma_{Ta_2O_5}$ = density of Ta_2O_5 (8.2 gm/cm^3)

ΔR = change in sheet resistivity after bake

R = initial sheet resistivity.

Calculation of contact resistance required accurate measurement of the total resistance of each pattern line. A model 3490A Hewlett Packard Digital Multimeter was used for this purpose. The sheet resistivity of the Au and Ta_2N films was calculated using the measured resistance values and dimensions of the solid Au and Ta_2N lines. (sheet resistivity = total resistance/number of squares). Contact resistance may be calculated from the formula

$$R_T = RS_{Au}\, S_{Au} + RS_{Ta_2N}\, S_{Ta_2N} + R_{SC}\, W_C\, N_C \tag{2}$$

where

R_T = total resistance of line

RS_{Au} = sheet resistivity of Au in ohms/square

S_{Au} = number of Au squares

RS_{Ta_2N} = sheet resistivity of Ta_2N in ohms/square.

S_{Ta_2N} = number of Ta_2N squares

R_{SC} = contact resistance in ohm mil/contact

W_C = width of contact in mils

N_C = number of contacts

The desired culmination of the experimental and calculated data is a final derived value representing a maximum storage life for Ta_2N thin films in air at ambient temperature and pressure. From the data shown in Figure 3, an aging relationship was deduced which took the form

$$\left(\frac{\Delta R}{R}\right)^n = Ae^{E_A/KT}\, t \qquad (3)$$

where

$\frac{\Delta R}{R}$ = the fractional resistance change

t = aging time

A = parameter dependent on processing and aging environment

T = aging temperature, ^oK

E_A = activation energy which experimentally ranged from[6,7] -0.6 to -1.2 eV

K = Boltzman's constant (8.6164×10^{-5} eV $^oK^{-1}$)

Previous thermal aging experiments[6] show n to equal 2, but as will be seen in the final analysis, (Equation 3B) the value of n has no bearing.

By manipulating this formula into a ratio of the form

$$\frac{\left(\frac{\Delta R}{R}\right)_1^n}{\left(\frac{\Delta R}{R}\right)_2^n} = \frac{Ae^{E_A/kT_1}\, t_1}{Ae^{E_A/kT_2}\, t_2} \tag{3A}$$

where subscript 1 represents conditions at ambient temperature and subscript 2 represents conditions at thermal aging temperature (in this study 300°C). When $\left(\frac{\Delta R}{R}\right)_1 = \left(\frac{\Delta R}{R}\right)_2$, this formula can be solved for t_1.

$$t_1 = \frac{t_2 e^{E_A/kT_2}}{e^{E_A/kT_1}} \tag{3B}$$

t_1 can now be calculated and defined as the aging time at ambient temperature T_1 necessary to form an oxide layer equal to that which is formed in time t_2 at temperature T_2 (300°C).

In addition, information on metallization adhesion quality was obtained directly from lead frame pull strengths. Gold plated copper alloy leads[8] were thermal compression bonded to gold bonding pads on the test pattern. The force needed to pull the leads (90° peel) from the substrate was measured and recorded.

RESULTS

Auger - Ion Sputter Profile

An ion sputter profile on one sample from each aging group clearly defined a direct relationship between thermal aging and oxide thickness. In each case there is a high concentration of oxygen at the surface of the film. (See Appendix for sputter profiles.) The initial sharp rise of oxygen is due to the elimination of organic surface contaminants. As the outer layers are sputter removed, the oxygen quickly drops off and the tantalum and nitrogen concentrations rise. The oxide and

Ta_2N film interface is difficult to determine from the profile, however, for the purpose of this study it will be defined as the point at which the oxygen and nitrogen profiles show a discernable slope change. This is graphically represented on the 3.5 hour profile contained in the appendix.

Figures 2A and 2B show the relationships between contact resistance and thermal aging time or oxide thickness respectively. Unless a sharp interface is present and the sputtering rate can be carefully controlled, AES/sputter profiling is not an accurate method of thickness determination and, therefore, the oxide thickness units are arbitrary.

Ion sputter profiling was also performed on samples which were exposed to atmospheric air and stored in a clean bench for 2, 26, 50, and 217 hours before analysis. A fifth sample was profiled which had been stored in a desk drawer for almost two years. There was no significant difference in oxide film thickness between these and samples analyzed immediately after deposition.

Oxide Thickness Measured by Ellipsometry and Calculations Based on Resistance

Ellipsometric measurements showed the oxide layer to vary in thickness from 19 Å to 80 Å depending upon length of thermal aging at 300°C (see Figure 3). The error inherent to this technique is estimated to be ± 10%.

Values of oxide thickness calculated from resistance data are in fair agreement with ellipsometric measurements even though a significant amount of scatter was observed. Values ranged from 27 Å to 80 Å (see Figure 3). The consistantly lower calculated values can presumably be attributed to (1) ellipsometric measurement error and (2) departure from the idealized geometry assumed for the calculations based upon resistance measurements. Due to scatter, either a parabolic or a linear growth rate can be fitted to the oxide thickness data.

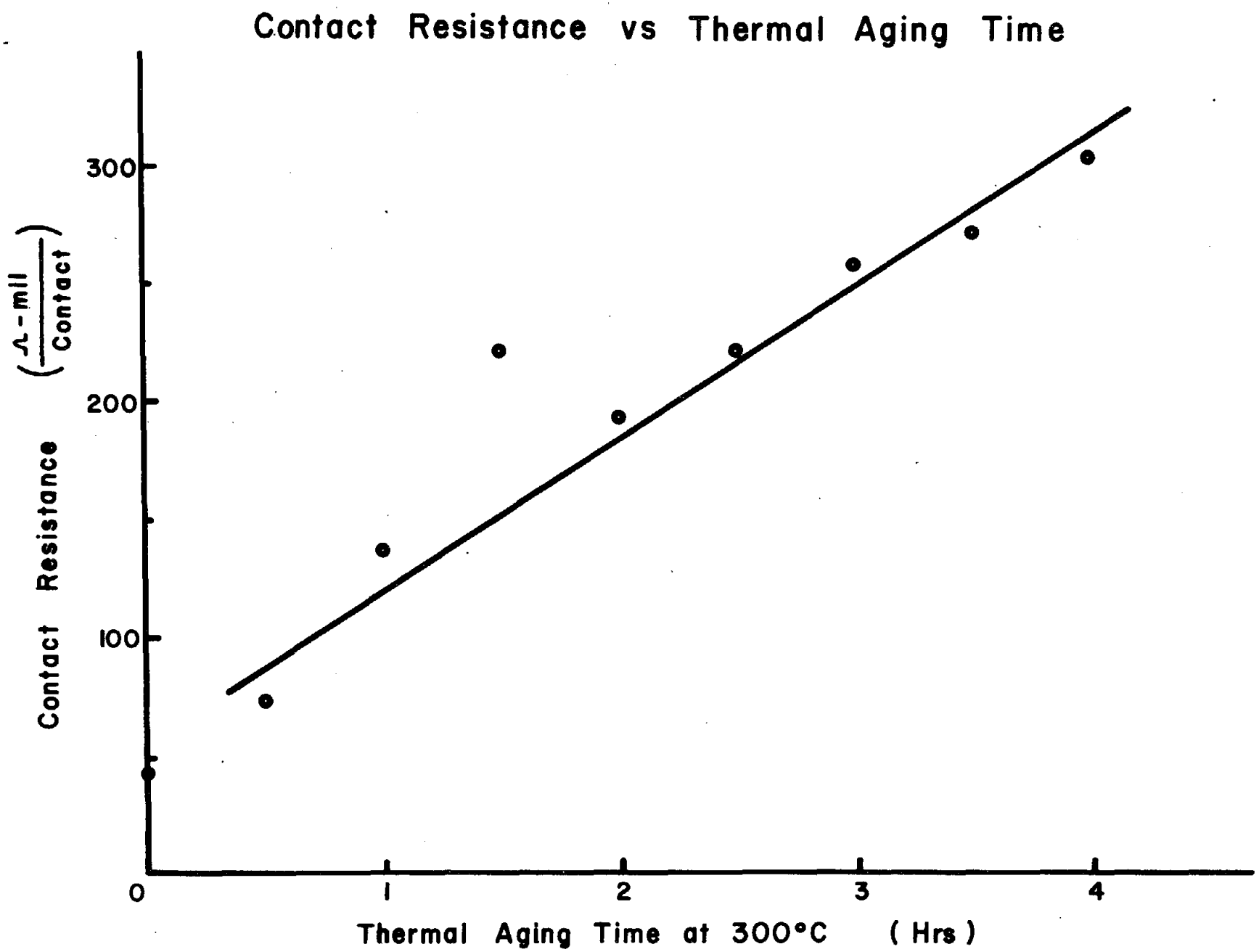

Contact Resistance vs Thermal Aging Time
Contact Resistance (Ω-mil / Contact)
300
200
100
0
1
2
3
4
Thermal Aging Time at 300°C (Hrs)

Figure 2A

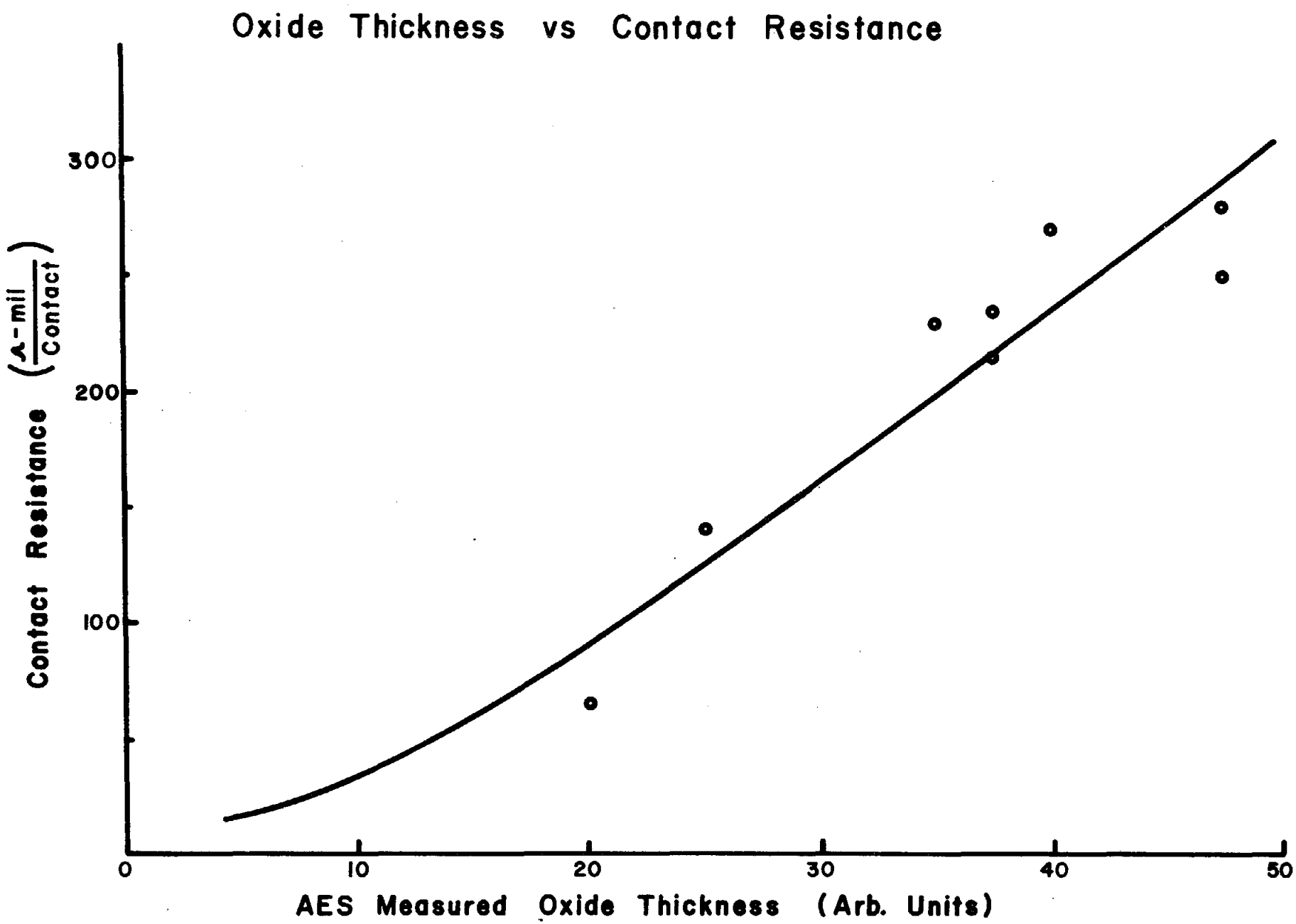

Oxide Thickness vs Contact Resistance
Contact Resistance (Ω-mil / Contact)
300
200
100
0
10
20
30
40
50
AES Measured Oxide Thickness (Arb. Units)

Figure 2B

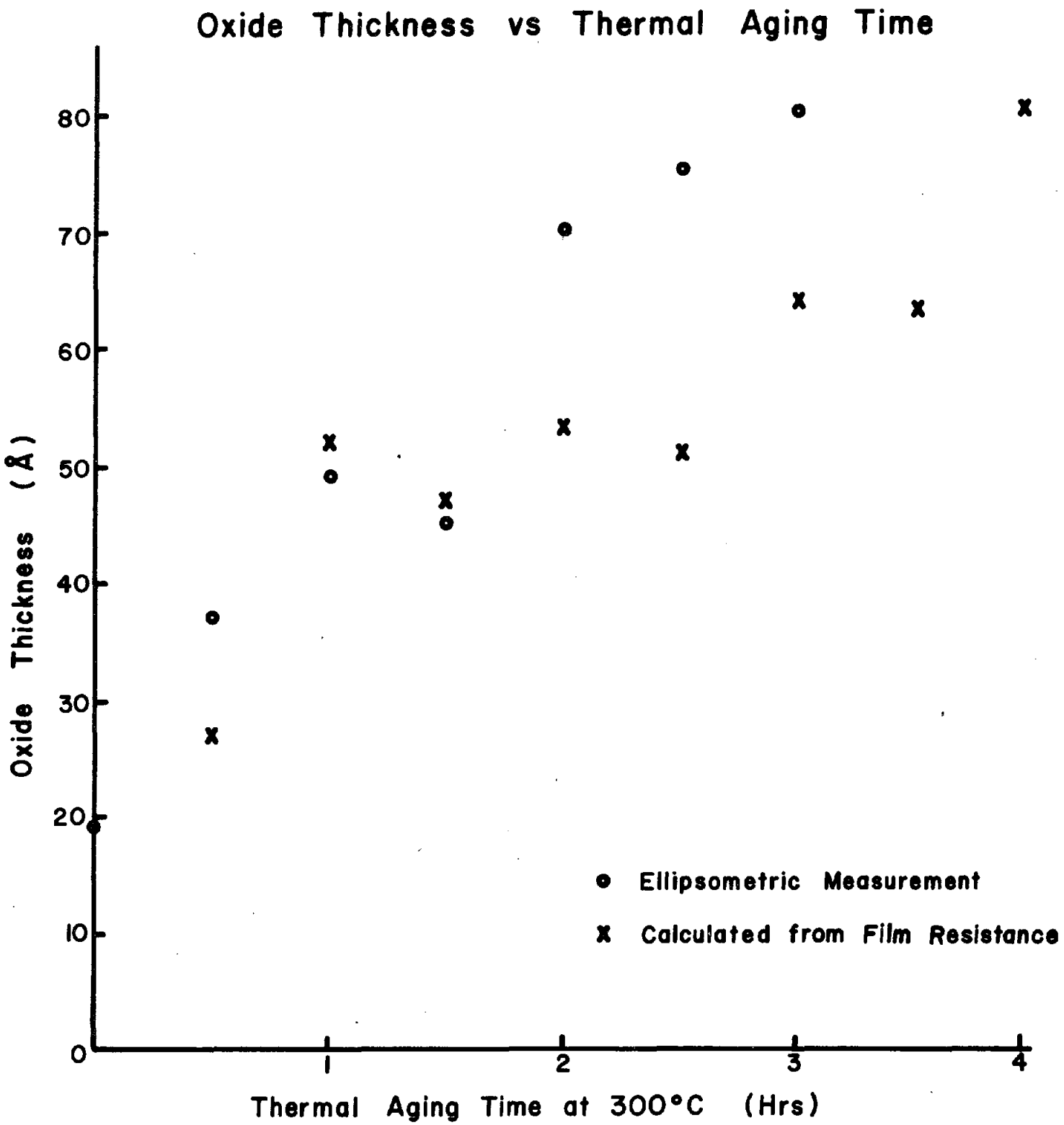

Oxide Thickness vs Thermal Aging Time
Oxide Thickness (Å)
80
70
60
50
40
30
20
10
0
1
2
3
4
Thermal Aging Time at 300°C (Hrs)
Ellipsometric Measurement
Calculated from Film Resistance

Figure 3

Adhesion

The average lead frame pull strengths were approximately equal to the strengths expected for this system[8] but as seen in Figure 4, the distribution bars showing maximum and minimum strengths are very wide. The average of the pull strengths did not vary much between samples. Failure modes were lead frame heel separation, gold-gold separation, and separation between substrate and metallization. There was not a single failure due to Ta_2N resistor and CrAu conductor separation. Also, there was no decrease in strength which could be attributed to aging.

DISCUSSION

One can estimate a maximum storage life for Ta_2N mirrors if an acceptable change in contact resistance can be defined. (Bondability may also be a consideration, but the data in this study indicates otherwise.) For example, if a 25% change in contact resistance could be allowed, this would be equivalent to an oxide thickness of 25 Å which is formed in 20 minutes of 300°C thermal aging in air. An activation energy of -0.6 eV represents the worst case condition and it is assumed this value does not change with temperature. It must also be assumed that all environmental constituents and rate controlling mechanism are the same for both ambient aging and thermal aging. Substitution of these time, temperature, and activation energy values into formula 3B yields a shelf life of approximately 3 years at atmospheric pressure and room temperature. Consideration must be given to surface contaminants other than oxides; therefore, storage environment should be free of organic contaminants with temperature not to exceed ambient. Another important precaution should be to cool the resistor films following deposition to as low a temperature as possible (preferrably to around 50°C) before exposure to atmospheric air.

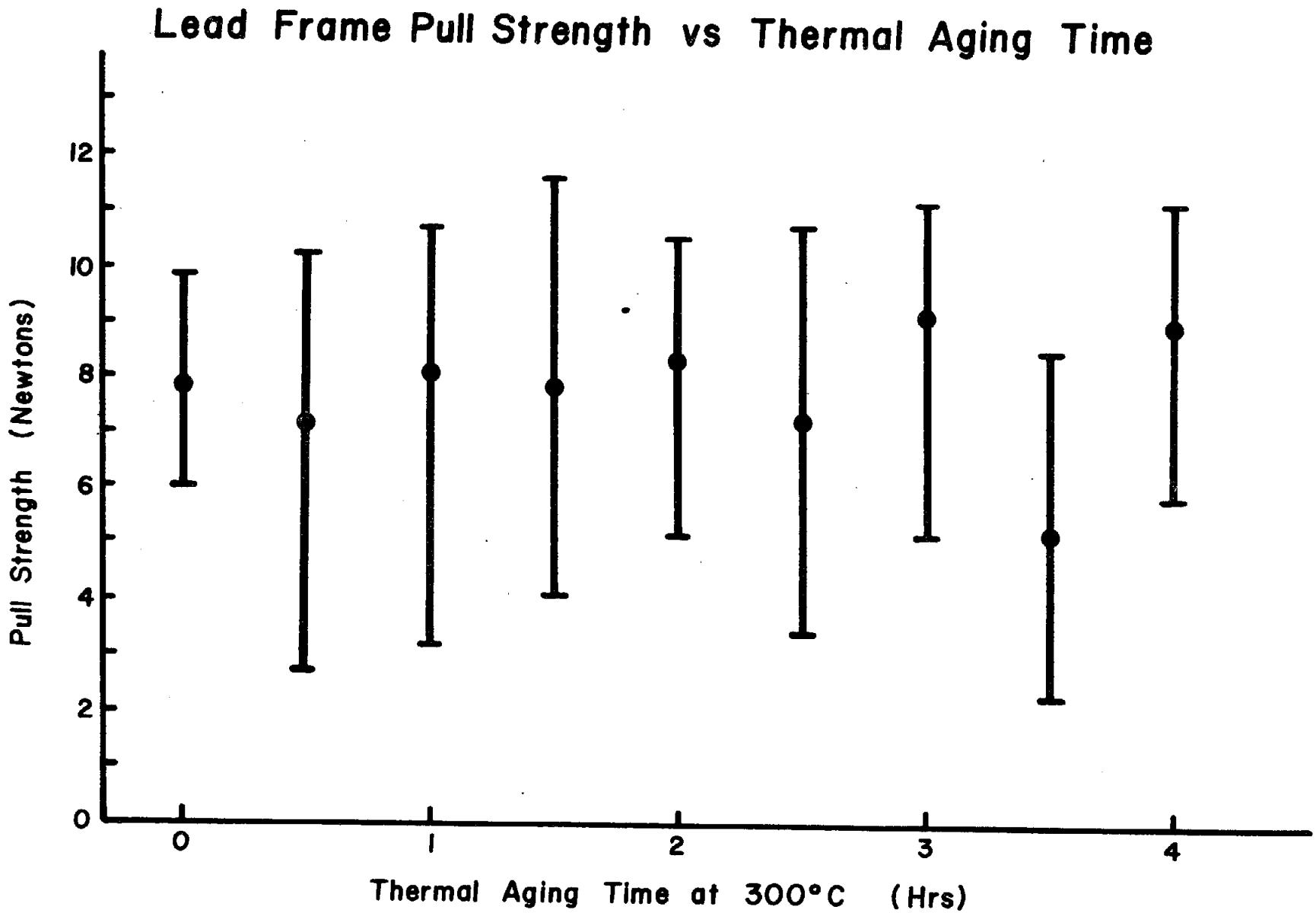

Lead Frame Pull Strength vs Thermal Aging Time
Pull Strength (Newtons)
0
2
4
6
8
10
12
0
1
2
3
4
Thermal Aging Time at 300°C (Hrs)

Figure 4

SUMMARY

A combination of Auger and Ellipsometry measurements with contact resistance measurements was made. The data combined with literature information[6,7] on oxidation rates, allows one to estimate a maximum Ta_2N mirror storage time for a defined change in contact resistance. Calculations show that allowing a 25% increase in contact resistance would allow storage of Ta_2N mirrors for approximately 3 years at 25°C. The limited data also indicates there is no change in metallization adhesion due to oxidation. However, before any change is made in the current specifications, these results should be verified. Also other problems such as contact noise and organic contamination should be investigated.

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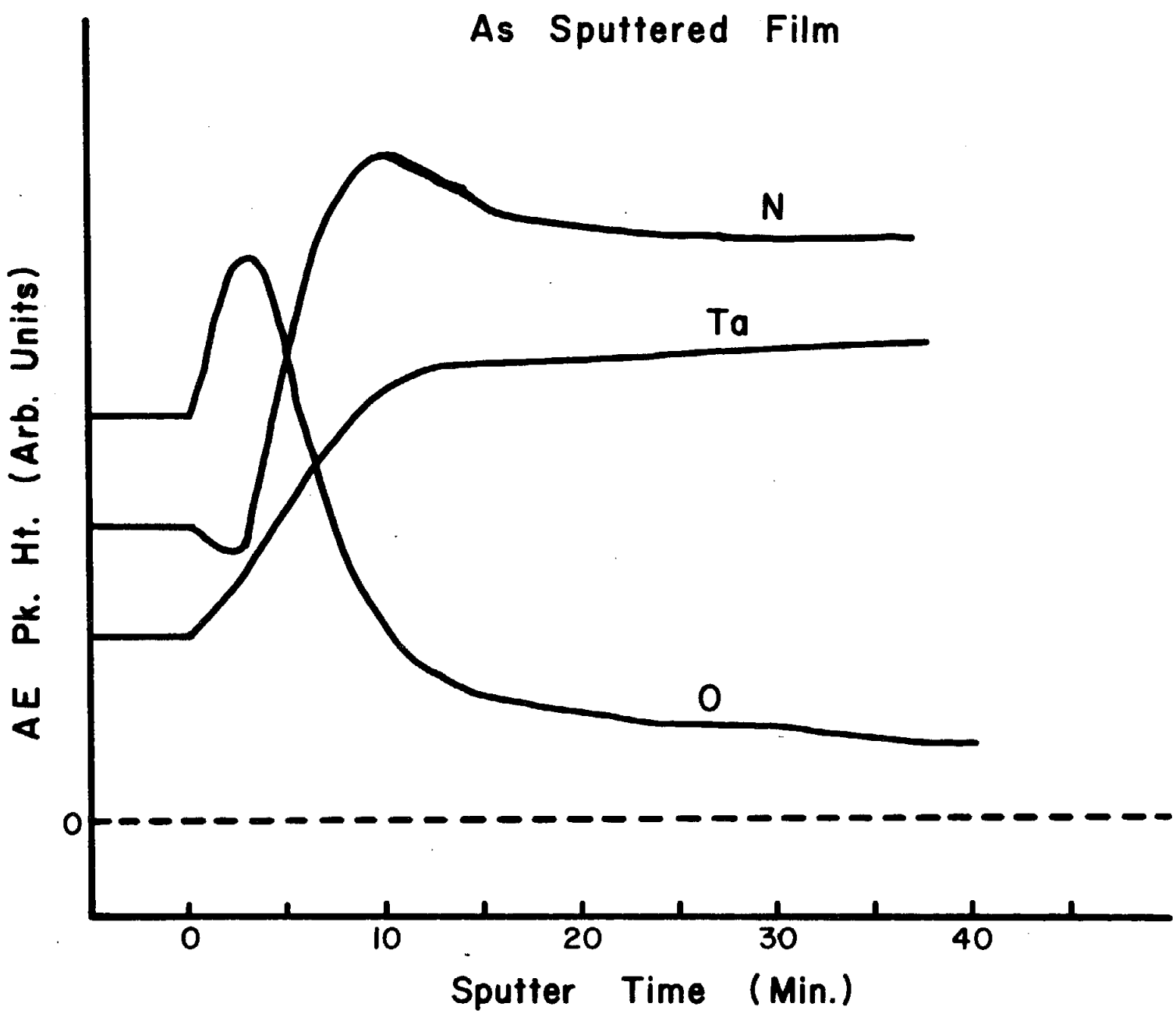
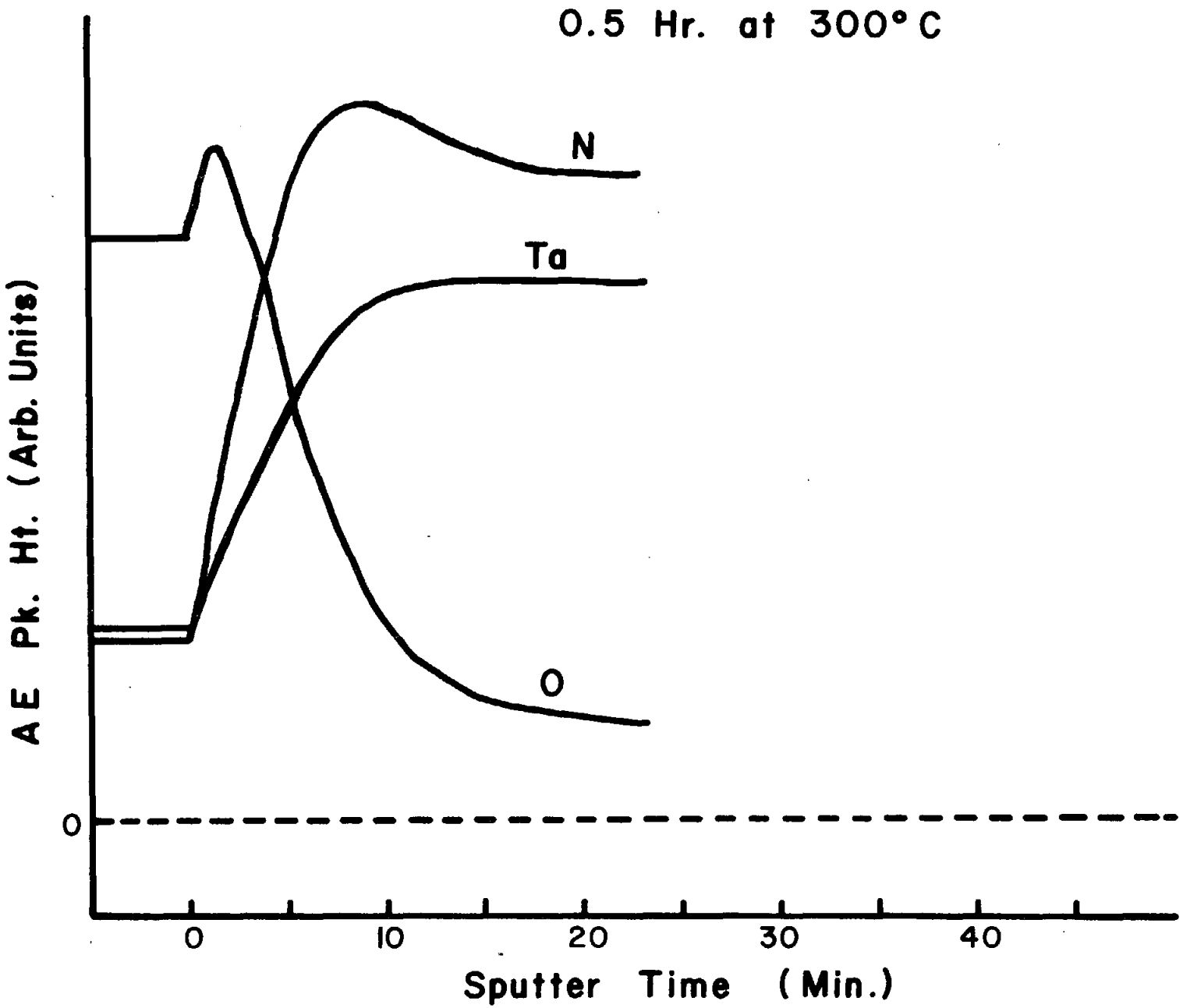
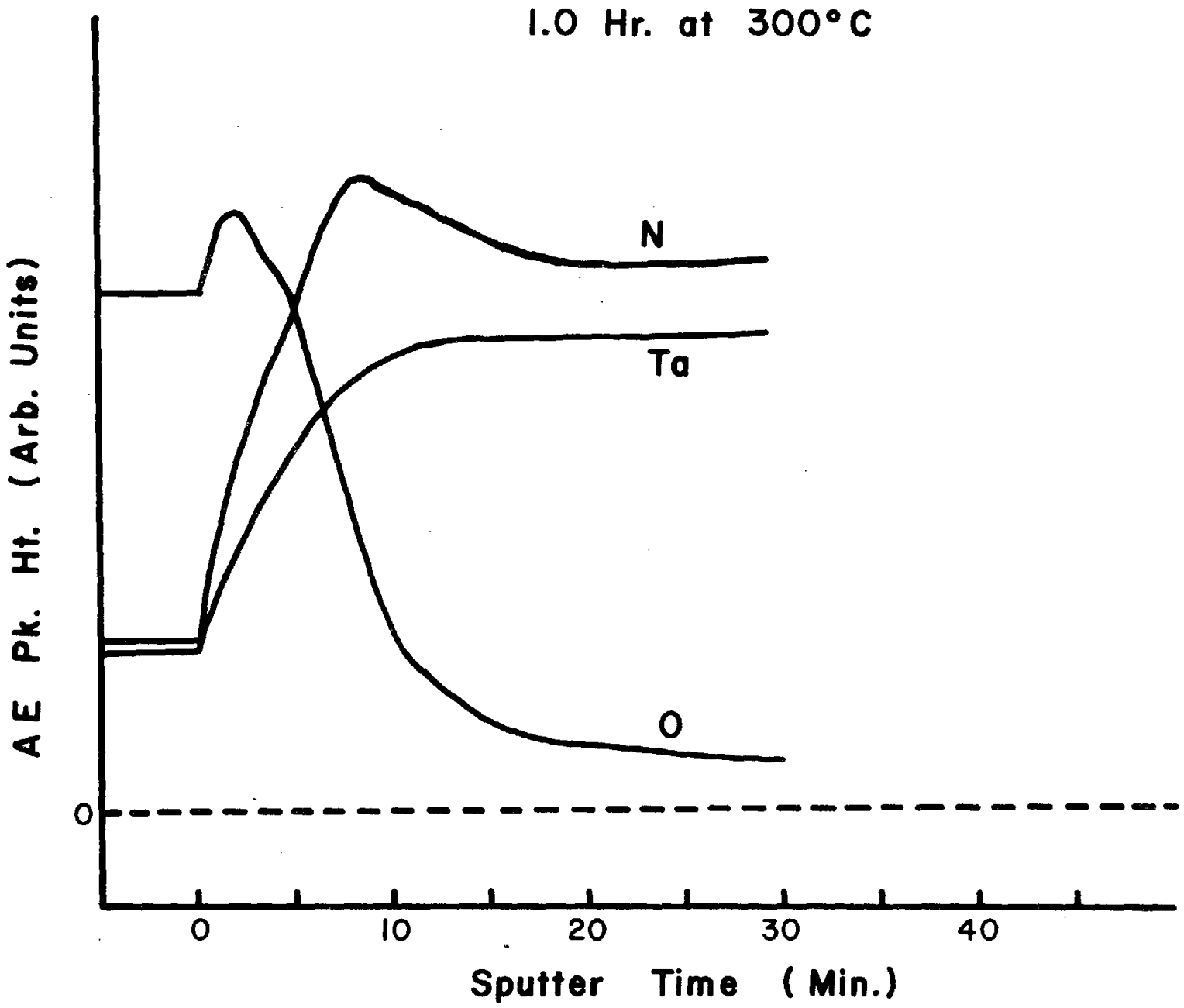
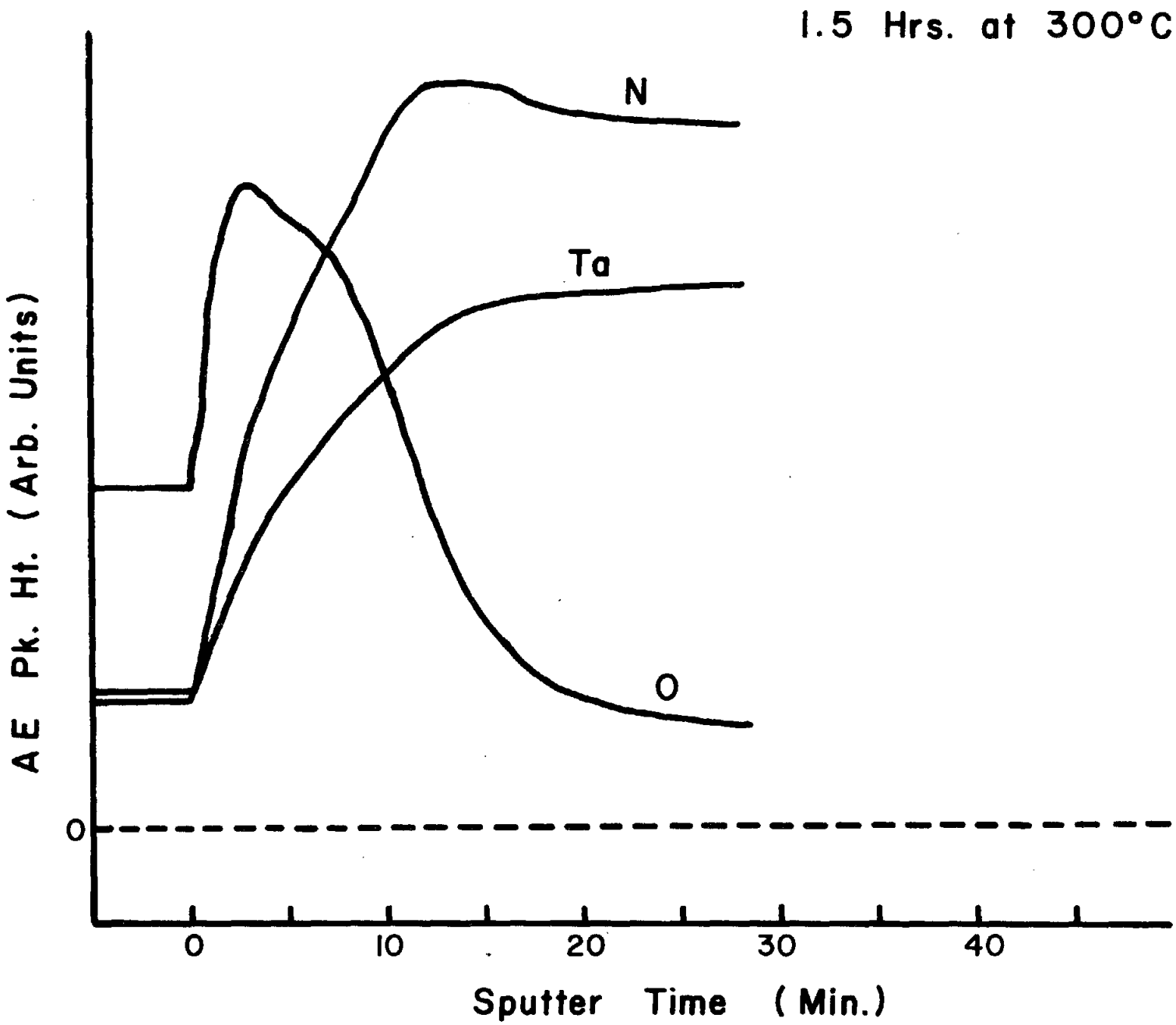
APPENDIX

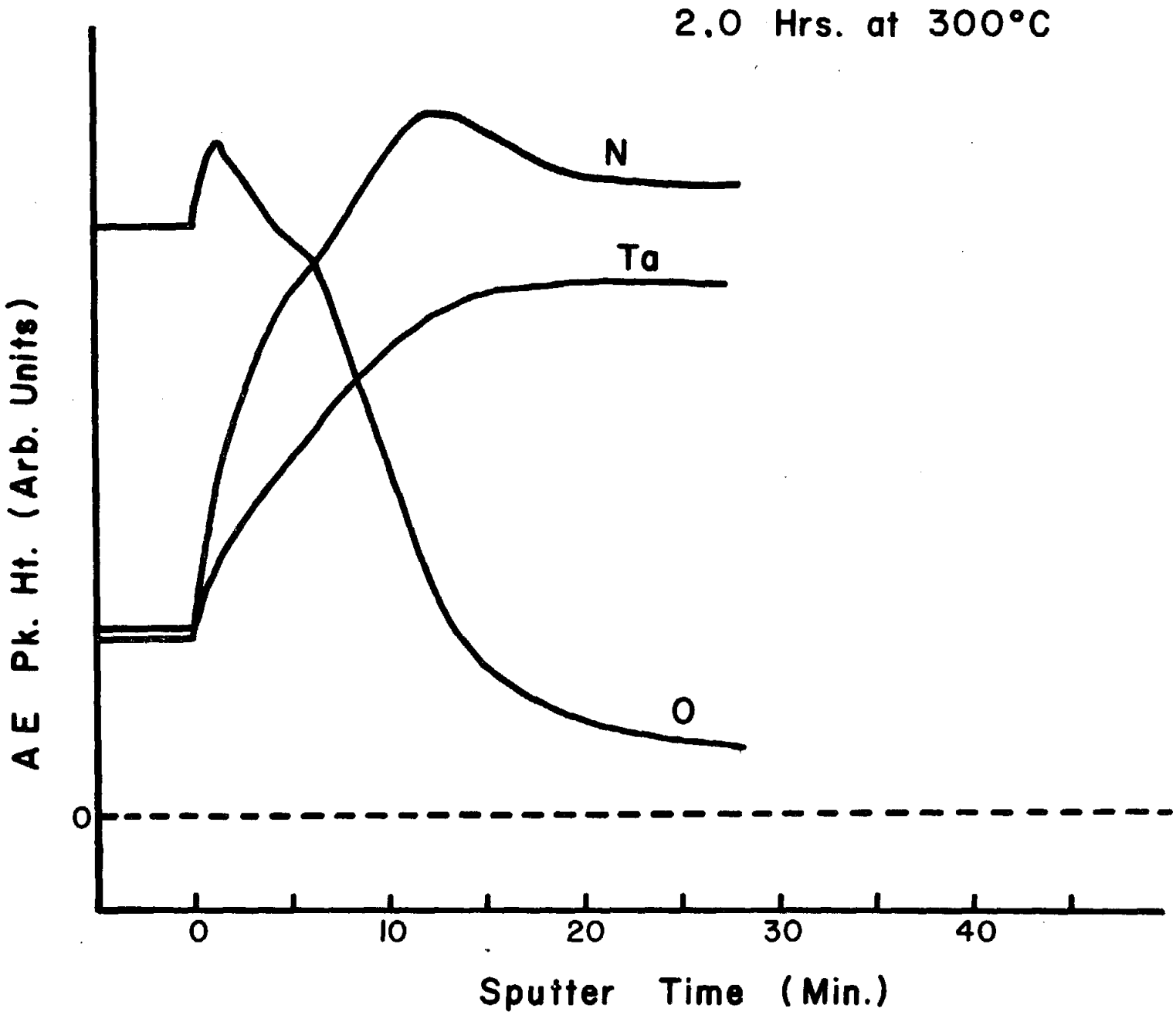
Auger Sputter Profiles showing the concentration behavior of tantalum, nitrogen and oxygen at the surface and down to approximately midway through the resistor films.

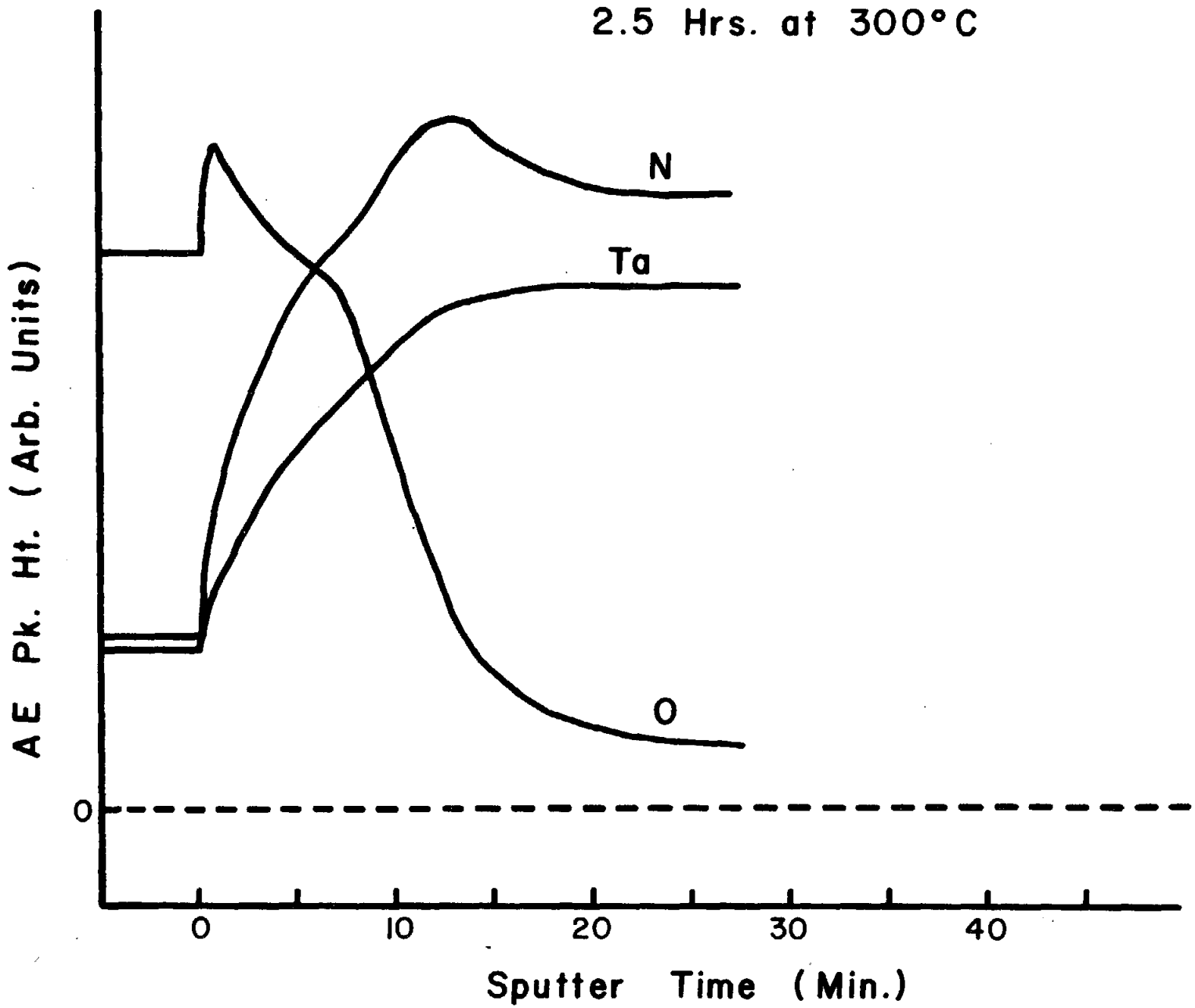

As Sputtered Film
N
Ta
O
AE Pk. Ht. (Arb. Units)
0
0
10
20
30
40
Sputter Time (Min.)

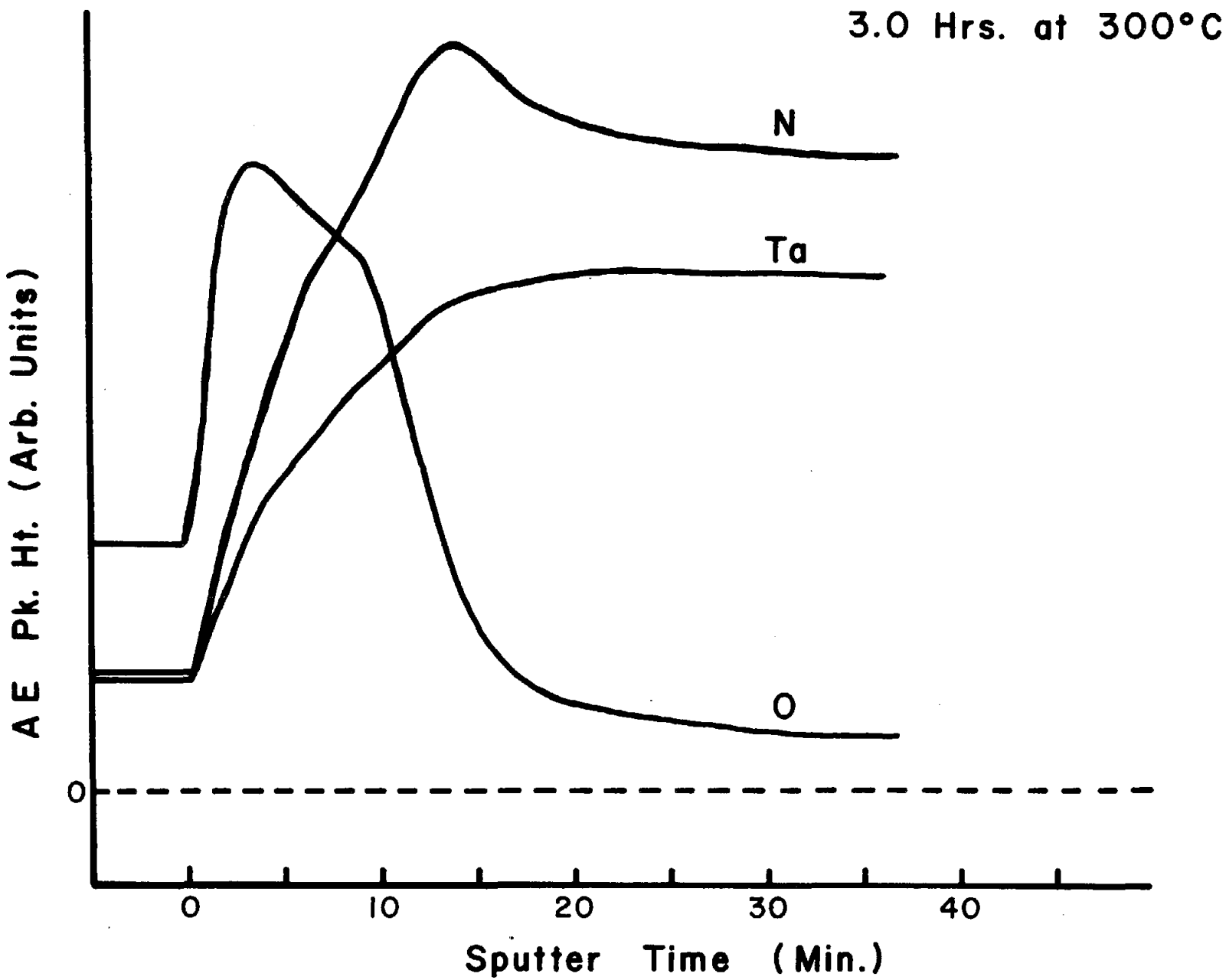

0.5 Hr. at 300° C
N
Ta
O
A E Pk. Ht. (Arb. Units)
0
0
10
20
30
40
Sputter Time (Min.)

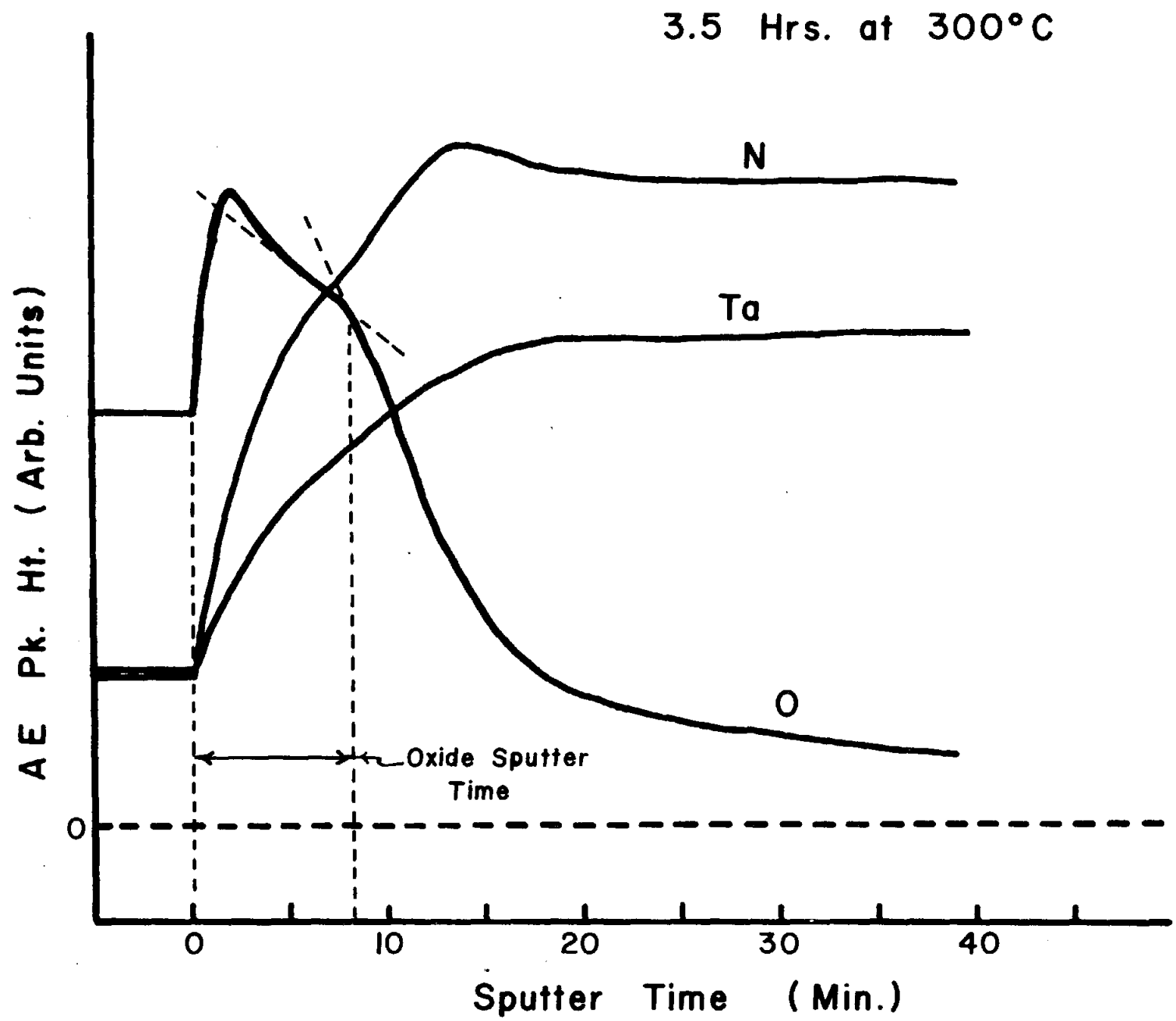

1.0 Hr. at 300°C
N
Ta
O
0
AE Pk. Ht. (Arb. Units)
0
10
20
30
40
Sputter Time (Min.)


1.5 Hrs. at 300°C
N
Ta
O
AE Pk. Ht. (Arb. Units)
0
0
10
20
30
40
Sputter Time (Min.)


2.0 Hrs. at 300°C
N
Ta
O
AE Pk. Ht. (Arb. Units)
0
0
10
20
30
40
Sputter Time (Min.)


2.5 Hrs. at 300°C
N
Ta
O
AE Pk. Ht. (Arb. Units)
0
0
10
20
30
40
Sputter Time (Min.)


3.0 Hrs. at 300°C
N
Ta
O
AE Pk. Ht. (Arb. Units)
0
0
10
20
30
40
Sputter Time (Min.)


3.5 Hrs. at 300°C
N
Ta
O
Oxide Sputter Time
AE Pk. Ht. (Arb. Units)
0
0
10
20
30
40
Sputter Time (Min.)

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