2

- NOTE -

THE MATERIAL INCLUDED IN THE FIRST PART OF THE TEXT HAS BEEN PREVIOUSLY REVIEWED FOR OPEN LITERATURE PUBLICATION AND WILL BE PRINTED IN APPLIED SPECTROSCOPY.

THE LATTER PORTION OF THE TEXT IS MORE RECENT DATA, BUT SIMILAR TO PREVIOUSLY PUBLISHED GEND DATA PRINTED IN JOURNAL OF VACUUM SCIENCE & TECHNOLOGY.

GEPP-OP-440

DEGRADATION STUDIES ON ERBIUM DIDEUTERIDE THIN FILMS

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ABSTRACT

Rare earth metals are used as hydrogen isotope occluders and function as electrodes in neutron generator tubes. In this study, erbium dideuteride thin films have been quantitatively measured for purity in order to establish the deleterious effects resulting from film processing. These processes include deposition, hydriding and neutron tube vacuum anneal. The data taken reveals that ~ 0.02 mg/cm^2 erbium metal is unavailable as the hydride due to surface oxidation and interfacial interactions between occluder metal and substrate.

1. INTRODUCTION

Thin film technology is important in many disciplines. A common problem encountered is the resulting purity of the deposited film. A contribution to this contamination is the interactions between the metal film and the substrate. Our particular interest is in erbium deuteride/tritide thin films, which are used for neutron generator electrodes.

The purity of the film strongly affects the neutron output. Previous studies[1-5] have shown significant losses of metal due to surface oxidation, which in turn reduces the purity of the hydride. The total metal lost and unavailable for hydriding would also include the metal lost to the interface.

In a previous study[6] using in situ tritide erbium films the total erbium unavailable for hydriding was quantitatively measured to be ∿ 0.01 mg/cm^2. It was determined that 0.004 mg/cm^2 was consumed as surface oxide and 0.006 mg/cm^2 was lost to the interface. Subsequent neutron tube processing is expected to further decrease the purity of the hydrided erbium film. The effects of these tube processes have not yet been determined. It is the intent of this work to quantitatively measure the purity of erbium dideuteride films which have been subjected to the entire tube processing sequence, which includes an extensive vacuum anneal.

The basic assumption made was that the effects of subsequent tube processing would further increase the surface oxide as compared with films which had not received this treatment. This increase in surface oxide would be reflected in the loading ratio (atoms of hydrogen isotopes/atoms of erbium) as film thickness expressed in areal density (milligrams per square centimeter) approached zero.

2. EXPERIMENTAL

2.1 Sample preparation

In this study, six film samples were prepared at 14 areal density levels. The film samples ranged in areal density from 0.01 mg/cm^2 to 0.5 mg/cm^2 and were made by means of electron beam deposition onto molybdenum substrates. The film sample size chosen was ∿ 2.54 cm in diameter in order to provide a large enough sample size for accurate gas and metal analysis. Immediately after deposition, purified deuterium was introduced into the vacuum chamber at 565 Pa (5 torr) pressure to form the dideuteride.[7] These films were in situ deuterided for two reasons. First, to reduce the level of surface oxidation,[8] and secondly, deuteride films are less susceptible to degradation as compared to tritided films.[9]

Using X-ray emission data, thirteen matched film pairs were chosen with major emphasis on areal densities below 0.1 mg/cm^2. One sample of the matched pair was selected for the control film, whereas the other was used as the processed film. This film was placed into a molybdenum tube envelope and subjected to vacuum anneal at 500°C for one hour.

2.2 X-ray emission

X-ray emission measurements were used to select pairs of film samples that were nearly identical over the areal density range. X-ray emission measurements were repeated after decomposing the hydride to determine any possible metal losses due to the degassing process or to detect metal remaining on the substrate after destructive analysis.

The spectrometer used in this study was a General Electric XRD-6 operated at 50 keV 50 mA using a LiF diffracting crystal. The erbium $L\alpha_1$ line was used for measuring the total metal.

2.3 Gas analysis

The erbium tritide films were thermally decomposed and the occluded gas measured by a DuPont 21-104 mass spectrometer. The analysis procedure for this decomposition has been reported elsewhere.[10]

2.4 Total metal analysis

The erbium metal was quantitatively measured by atomic absorption using a Perkin Elmer 403 spectrophotometer. A nitrous-oxide/acetylene flame was used for atomization and the erbium 4008 A resonance line was monitored. The erbium films were quantitatively dissolved from the substrate using a dilute hydrochloric acid solution and procedure previously reported.[11]

2.5 Experimental procedure

In a previous study[6] it was shown that the metal unavailable for hydriding (for in situ hydrided films) resulted primarily from surface oxidation and interaction between the occluder metal and the substrate. This effect becomes more evident in the loading ratio as the film areal density approaches zero. In this work, it was expected that further film degradation would occur particularly during the vacuum anneal at 500°C for one hour. The data verified this assumption.

3. RESULTS AND DISCUSSIONS

Experimental results taken on both the vacuum annealed and non-annealed specimens are presented in Table I. Also included in Table I are the calculated loading ratios from these data using only deuterium only as well as both protium and deuterium. Loading ratio refers to the ratio of the hydrogen isotope atoms to erbium metal atoms.

In Figure 1, the X-ray intensities of the thirteen erbium film pairs are plotted against their experimentally determined areal densities. As illustrated by Figure 1, the film samples chosen show good correlation to the X-ray intensities with virtually no scatter.

Figure 2 is a plot of the loading ratio obtained using protium plus deuterium versus the film areal densities for both annealed and non-annealed specimens. The annealed samples were selected erbium dideuteride films that were placed into molybdenum tube envelopes and subjected to vacuum anneal at 500°C for one hour. As evidenced by the data, there is a definite loss in hydrogen isotope content for the film specimens subjected to this process. Since protium has been reported to be a variable in the film processing,[12] (e.g., hydriding, vacuum anneal) an alternative presentation of the data would be a similar plot of the loading ratio versus areal density using only deuterium. These data are given in Figure 3 and show the gas loss resulting from vacuum anneal in a similar but more defined curve with less scatter.

To clearly show the effects of vacuum anneal, a plot showing micron liters of deuterium versus areal density is presented in Figure 4. A well defined linear relationship is obtained for both the control specimens and the annealed specimens. The intercept of these two curves on the areal density axis corresponds to the erbium metal that is unavailable for hydriding. The control specimens show ~ 0.01 mg/cm^2 metal nonhydrided and compares well with previous reported work.[6] The vacuum annealed specimens show ~ 0.02 mg/cm^2 metal nonhydrided. This is more evident in Figure 5 which is an expanded plot of the data for the lower areal density films. The data clearly shows an increase of ~ 0.01 mg/cm^2 nonhydrided metal results from the annealing process.

The total unavailable metal for the non-annealed specimen if converted to total oxide would be ∿ 115 Å. However, previous work[8] reported that ∿ 50 Å could be attributed to surface oxide for in situ hydrided films. Therefore, the remainder of the metal is lost to the interface, free metal or other compounds. For the annealed samples, the increased metal loss when calculated as oxide loss is equivalent to an additional ∿ 115 Å. This would be in addition of the 50 Å previously reported[8] and would give a total oxide level for the annealed films of 165 Å.

4. CONCLUSIONS

Fundamental techniques have been used to quantitatively measure the purity of erbium dideuteride thin films resulting from specific processing of neutron generator tubes.

These data are necessary in assessing the quality of the electrode which, in turn, can affect total neutron output of the generator.

It has been determined that ∿ 0.01 mg/cm^2 of erbium is not hydrided for films that were electron beam deposited and in situ hydrided. These data confirm previous results.[6] Measurements of the surface oxide show approximately 50 Å for in situ hydrided films. This would correspond to ∿ 0.004 mg/cm^2 as erbium oxide and ∿ 0.006 mg/cm^2 lost to the interface and/or other compounds of erbium.

The erbium film samples subjected to vacuum anneal at 500°C for one hour exhibited a total nonhydrided metal quantity of ∿ 0.02 mg/cm^2. This represents an additional increase of 0.01 mg/cm^2 nonhydrided metal resulting from the vacuum anneal process. If this quantity of metal were consumed as surface oxide, this would be an increase of ∿ 115 Å of oxide in addition to the 50 Å already present on the film, or a total surface oxide level of ∿ 165 Å.

The data also show that effects of surface oxidation on the loading ratio are minimal for films with areal densities greater than 0.3 mg/cm^2 and again agree with previously reported data.[6]

ACKNOWLEDGMENTS

The authors greatly appreciate the film preparation by J. L. Provo, the X-ray data by E. N. Kling and the mass spectrometer data by J. F. Kohls.

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11 Unpublished data.

12 Unpublished data.

FIGURE CAPTIONS

1. Figure 1 - X-ray Intensity of the Erbium $L\alpha_1$ Line Versus Film Areal Density.

2. Figure 2 - Loading Ratio Using Protium Plus Deuterium Versus Film Areal Density for Both Annealed and Non-annealed Specimens.

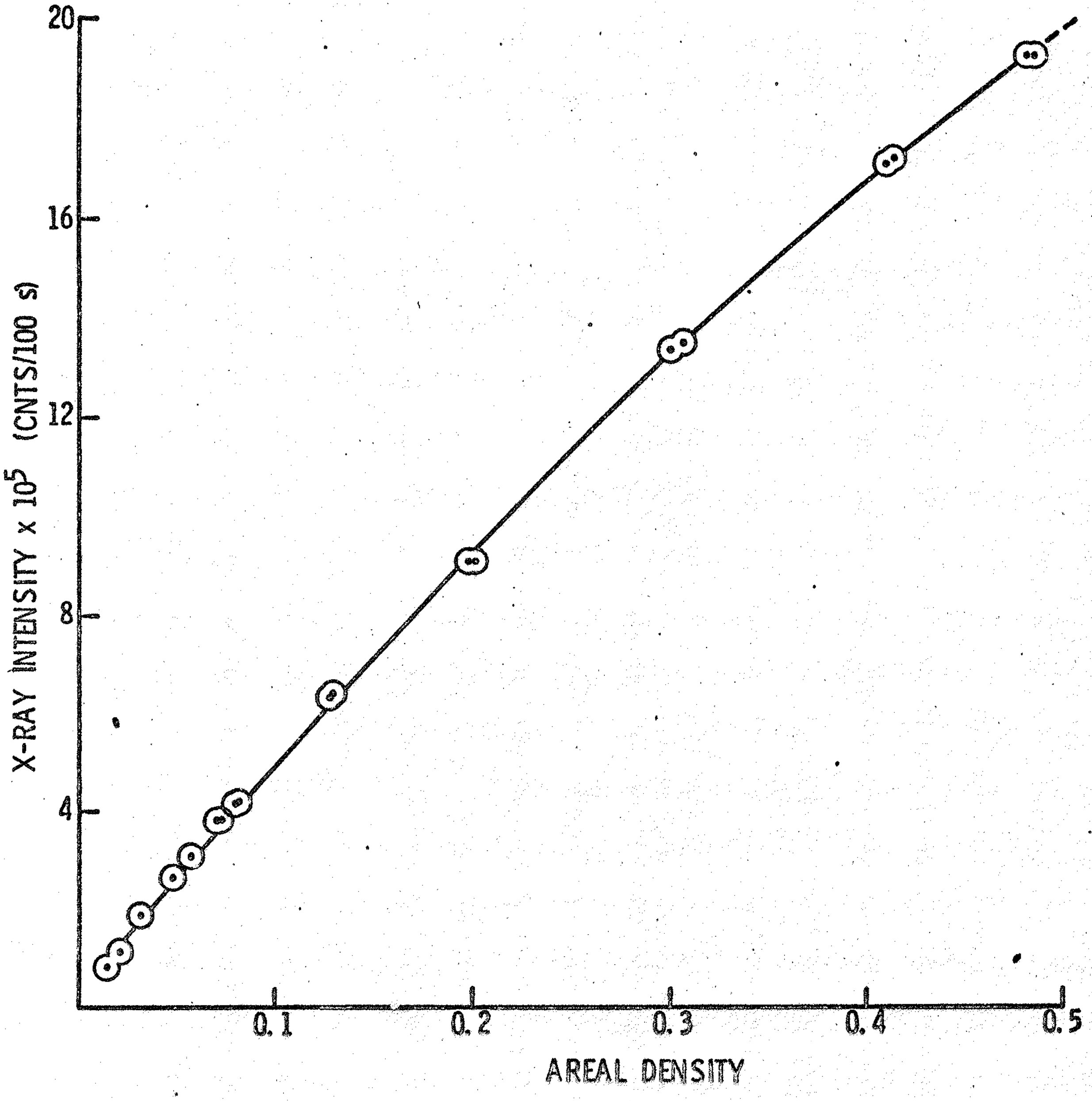
3. Figure 3 - Loading Ratio Using Deuterium Only Versus Film Areal Density for Both Annealed and Non-annealed Specimens.

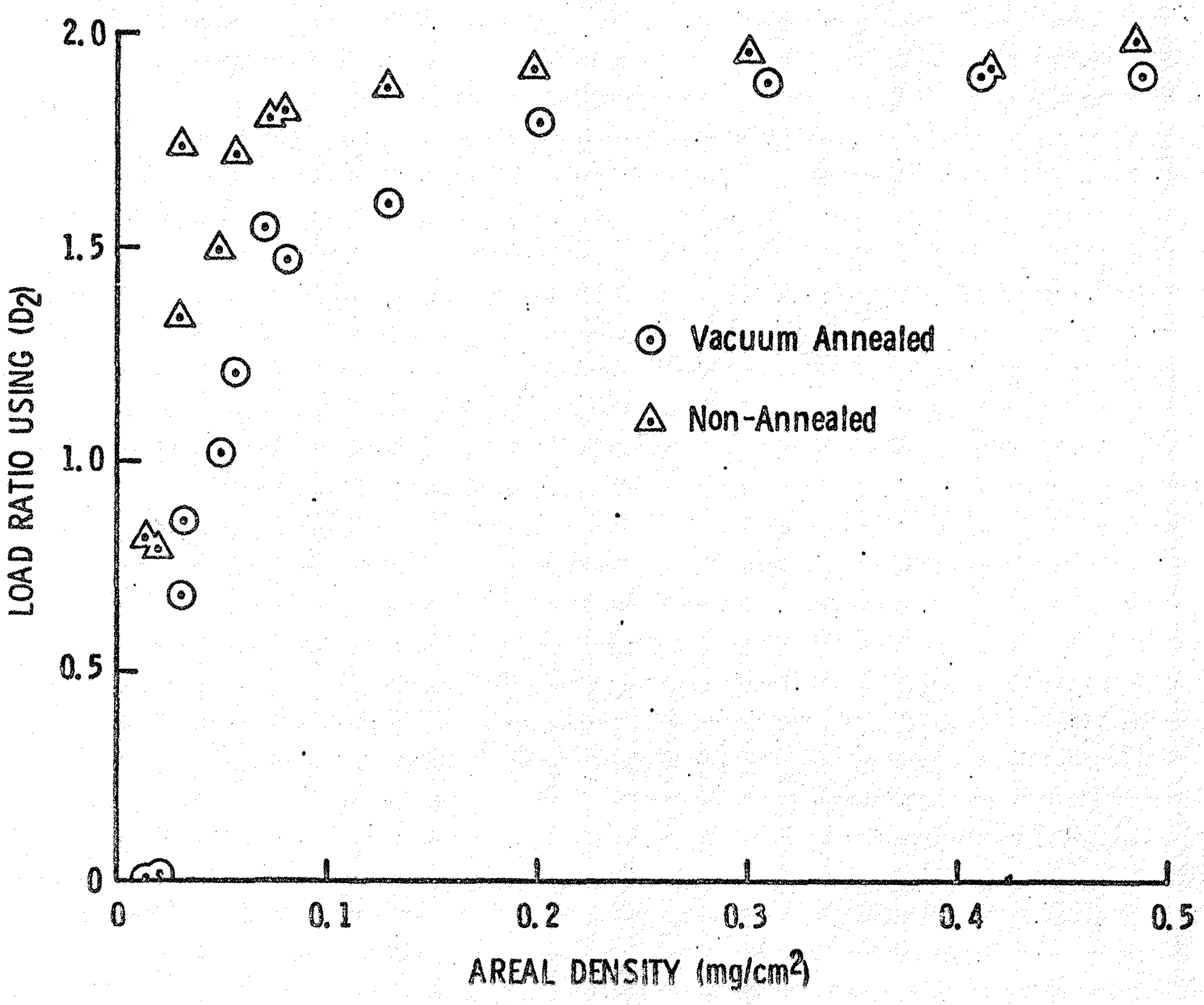
4. Figure 4 - Micron Liters of Deuterium Versus Film Areal Density for Both Annealed and Non-annealed Specimens.

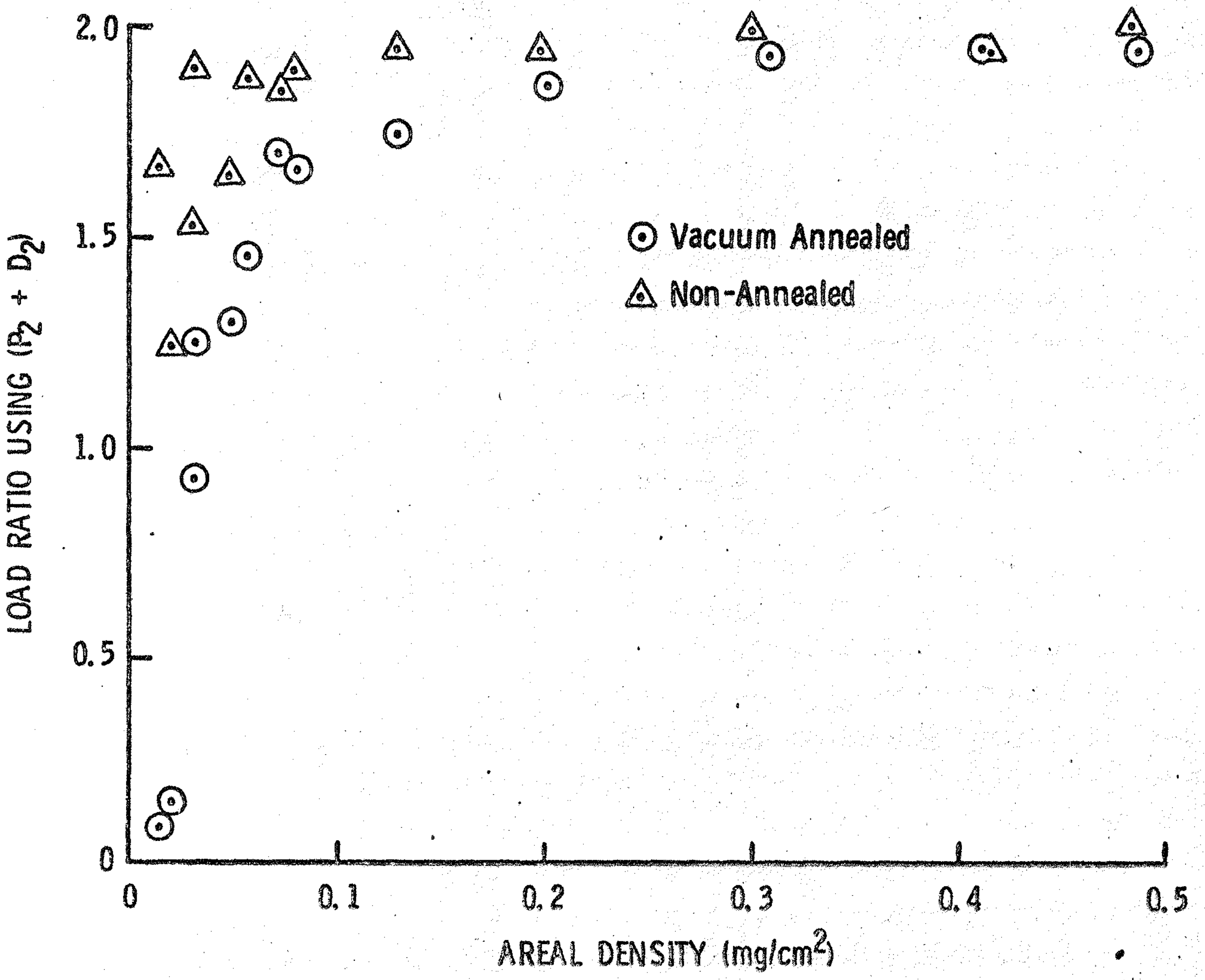
5. Figure 5 - Micron Liters of Deuterium Versus Film Areal Density for Both Annealed and Non-annealed Specimens on an Expanded Scale.

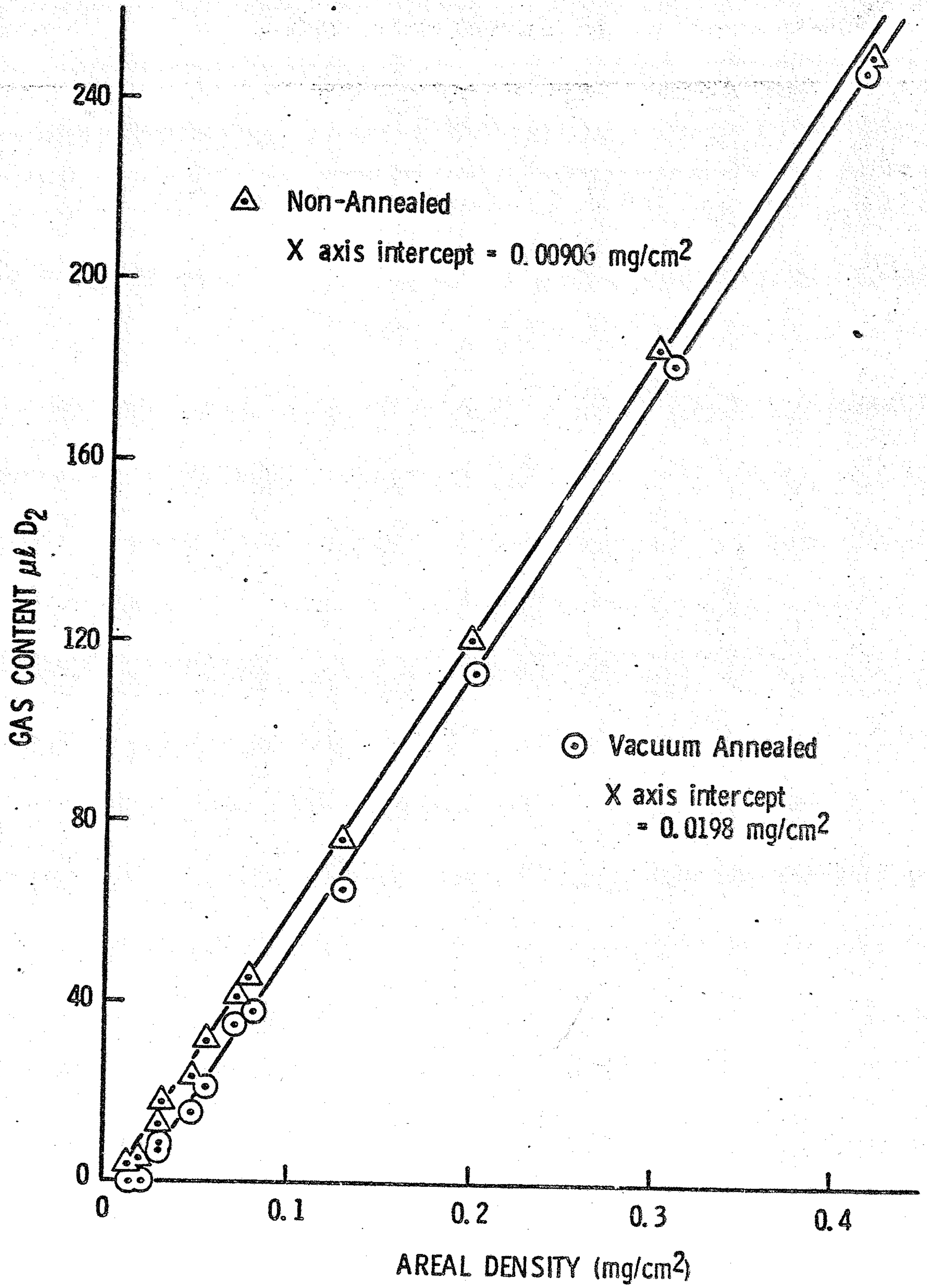
TABLE CAPTION

Table I. A Summary of All Data Taken on Film Specimens, Both Annealed and Non-annealed.


20
16
12
8
4
X-RAY INTENSITY x 10^5 (CNTS/100 s)
0.1
0.2
0.3
0.4
0.5
AREAL DENSITY


2.0
1.5
1.0
0.5
0
LOAD RATIO USING (D_2)
0
0.1
0.2
0.3
0.4
0.5
AREAL DENSITY (mg/cm^2)
⊙ Vacuum Annealed
△ Non-Annealed


2.0
1.5
1.0
0.5
0
0
0.1
0.2
0.3
0.4
0.5
LOAD RATIO USING ($P_2 + D_2$)
AREAL DENSITY (mg/cm^2)
⊙ Vacuum Annealed
△ Non-Annealed



Non-Annealed
X axis intercept = 0.00906 mg/cm^2
Vacuum Annealed
X axis intercept = 0.0198 mg/cm^2
GAS CONTENT $\mu\ell$ D_2
240
200
160
120
80
40
0
0
0.1
0.2
0.3
0.4
AREAL DENSITY (mg/cm^2)

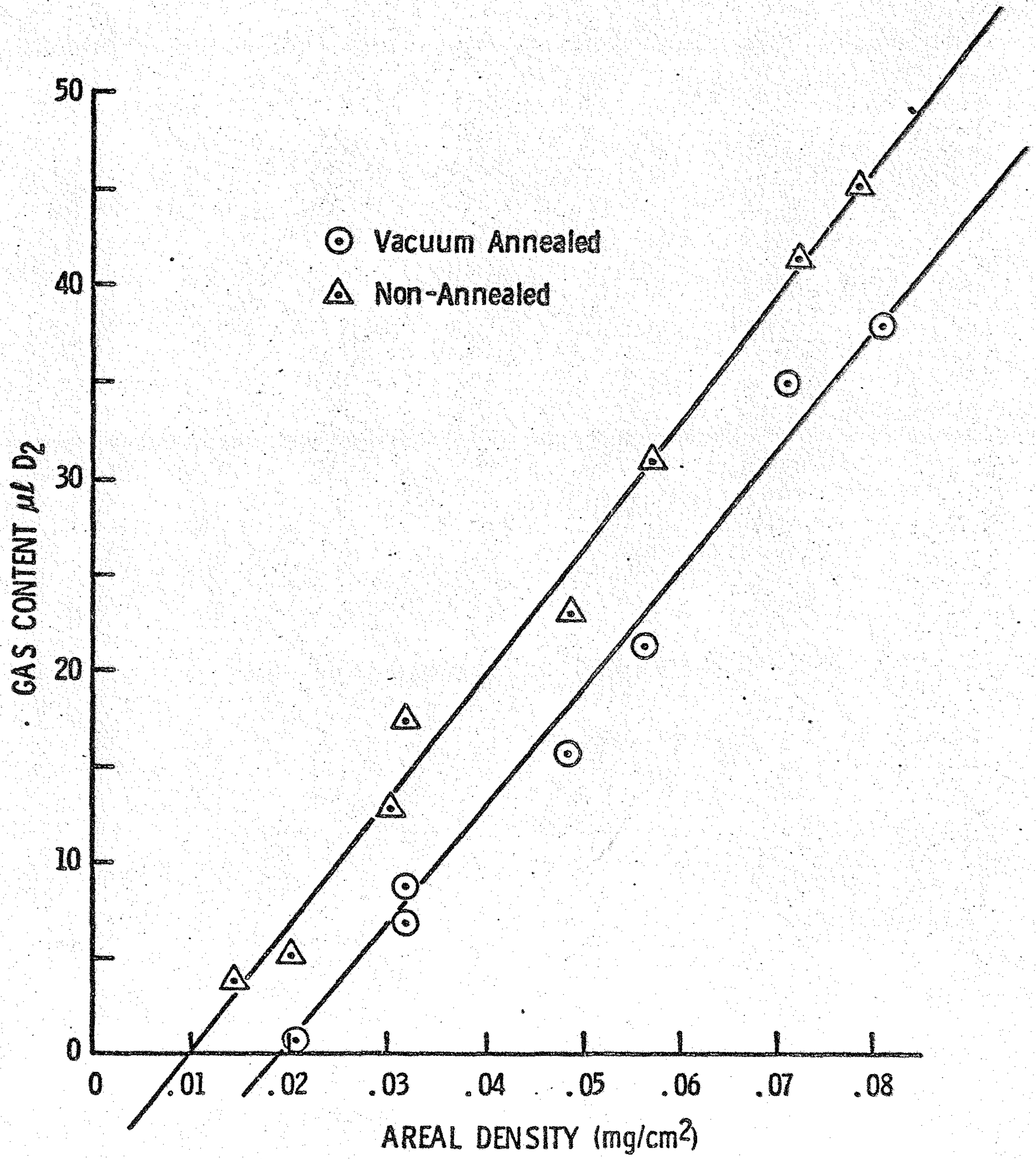

⊙ Vacuum Annealed
△ Non-Annealed
GAS CONTENT μl D_2
50
40
30
20
10
0
0
.01
.02
.03
.04
.05
.06
.07
.08
AREAL DENSITY (mg/cm^2)

Table I. A Summary of All Data Taken on Film Specimens, Both Annealed and Non-annealed

Sample Number	Vacuum Anneal	X-ray Intensity Counts/ 100 s	Total Metal (mg)	Areal Density (mg/cm^2)	P_2 (µℓ)	D_2 (µℓ)	Load Ratio I*	Load Ratio II**
1	Yes	85883	0.0816	0.0143	0.39	0.01	0.0022	0.0891
2	No	85872	0.0816	0.0143	3.72	3.78	0.842	1.67
3	Yes	116944	0.117	0.0205	0.85	0.08	0.0124	0.144
4	No	114460	0.116	0.0203	2.87	5.02	0.786	1.24
5	Yes	187538	0.181	0.0317	2.39	6.80	0.683	0.923
6	No	184590	0.173	0.0303	1.87	12.67	1.33	1.53
7	Yes	188978	0.182	0.0318	3.91	8.59	0.858	1.25
8	No	189632	0.183	0.0319	1.74	17.43	1.73	1.90
9	Yes	266555	0.276	0.0483	4.15	15.56	1.02	1.30
10	No	263854	0.278	0.0487	2.48	22.82	1.49	1.65
11	Yes	308169	0.322	0.0563	4.75	21.06	1.19	1.46
12	No	305854	0.327	0.0571	3.14	30.76	1.71	1.88
13	Yes	383966	0.411	0.0712	4.04	34.75	1.54	1.71

*Load Ratio I is calculated using micron liter (µℓ) of D_2.

**Load Ratio II is calculated using micron liter (µℓ) of D_2 + P_2.

Table I (Continued). A Summary of All Data Taken on film Specimens, Both Annealed and Non-annealed

Sample Number	Vacuum Anneal	X-ray Intensity Counts/ 100 s	Total Metal (mg)	Areal Density (mg/cm^2)	P_2 ($\mu\ell$)	D_2 ($\mu\ell$)	Load Ratio I*	Load Ratio II**
14	No	381515	0.416	0.0726	1.28	41.13	1.80	1.85
15	Yes	417532	0.466	0.0813	4.95	37.73	1.47	1.66
16	No	418088	0.450	0.0787	1.95	45.06	1.82	1.90
17	Yes	636835	0.739	0.129	5.49	65.14	1.60	1.74
18	No	633963	0.733	0.128	3.15	75.31	1.87	1.94
19	Yes	915792	1.149	0.201	4.31	113.27	1.79	1.86
20	No	913178	1.138	0.198	1.84	119.96	1.92	1.94
21	Yes	1342022	1.763	0.308	5.69	181.55	1.87	1.93
22	No	1323265	1.715	0.301	3.20	184.93	1.96	1.99
23	Yes	1698679	2.362	0.412	6.38	247.16	1.90	1.95
24	No	1692388	2.382	0.415	3.48	251.23	1.92	1.94
25	Yes	1913239	2.784	0.487	6.85	290.49	1.90	1.94
26	No	1915582	2.796	0.484	3.99	304.79	1.98	2.01

*Load Ratio I is calculated using micron liter ($\mu\ell$) of D_2.

**Load Ratio II is calculated using micron liter ($\mu\ell$) of $D_2 + P_2$.

DEGRADATION STUDIES OF ScD_2 THIN FILM

By: D. M. Holloway

A good deal of interest has been shown with regard to oxygen regrowth on in-situ deuterided scandium films that have been sputter cleaned. This condition may closely simulate the electrode (after acceptance operation). Film samples studied were sputter cleaned using Argon ions and then allowed to sit in vacuum 5×10^{-10} torr for several hours receiving approximately 36 Langmiur exposure. The samples were then analyzed for oxide using Auger/sputter techniques. These data are summarized in Figures 1 and 2. As evidenced by the data, an oxide layer near 26Å was regrown on the sputter cleaned surface. A previous hypothesis had suggested that very little oxide growth would occur, however, these data did not support the hypothesis.

Other information was also inferred with regard to the kinds of gases interacting with the sputter cleaned surface as evidenced by Figures 3 and 4. Note the very large carbon signal on the sputter cleaned regrown specimen which suggests an interaction of the film with a carbon bearing species.

The native oxide on these films was measured by Harris at Sandia and showed approximately 60Å, all within 4% of one another.

Data was also taken on a sputter cleaned ScD_2 film exposed to laboratory air for one hour. The Auger/sputter depth profile data showed that the surface oxide grew to a level greater than the native oxide. However, it is not yet clear if sputtering the specimen increased the surface area thus giving rise to an apparent high oxygen signal as suggested by Harris. However, experiments are presently underway to make these determinations. The data for this particular film is presented in Figure 5.

Finally, work regarding oxidation of electrodes will be reported as it becomes available.

Figure 1

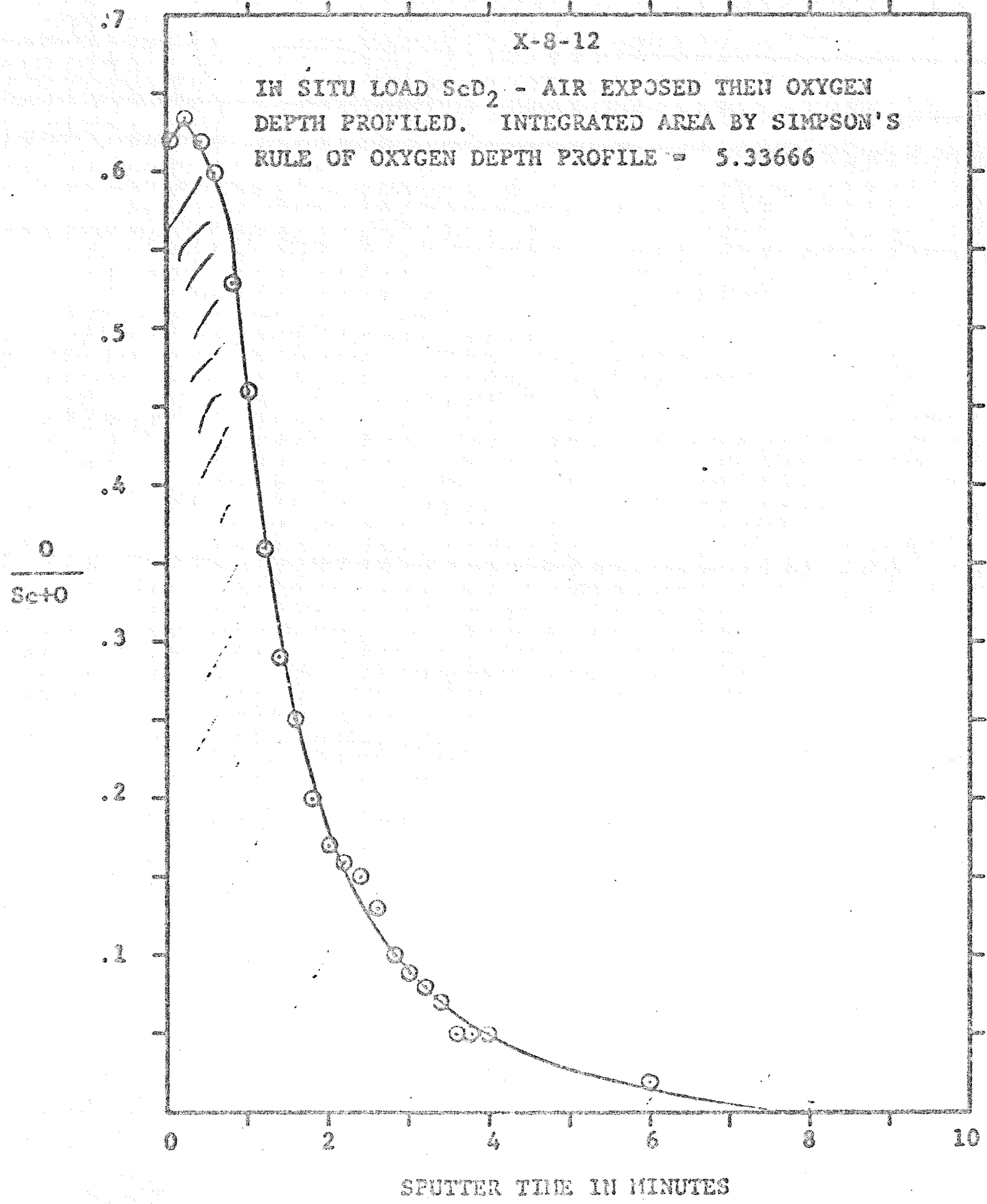

X-8-12
IN SITU LOAD ScD_2 - AIR EXPOSED THEN OXYGEN DEPTH PROFILED. INTEGRATED AREA BY SIMPSON'S RULE OF OXYGEN DEPTH PROFILE = 5.33666
.7
.6
.5
.4
.3
.2
.1
$\frac{O}{Sc+O}$
0
2
4
6
8
10
SPUTTER TIME IN MINUTES

Figure 2

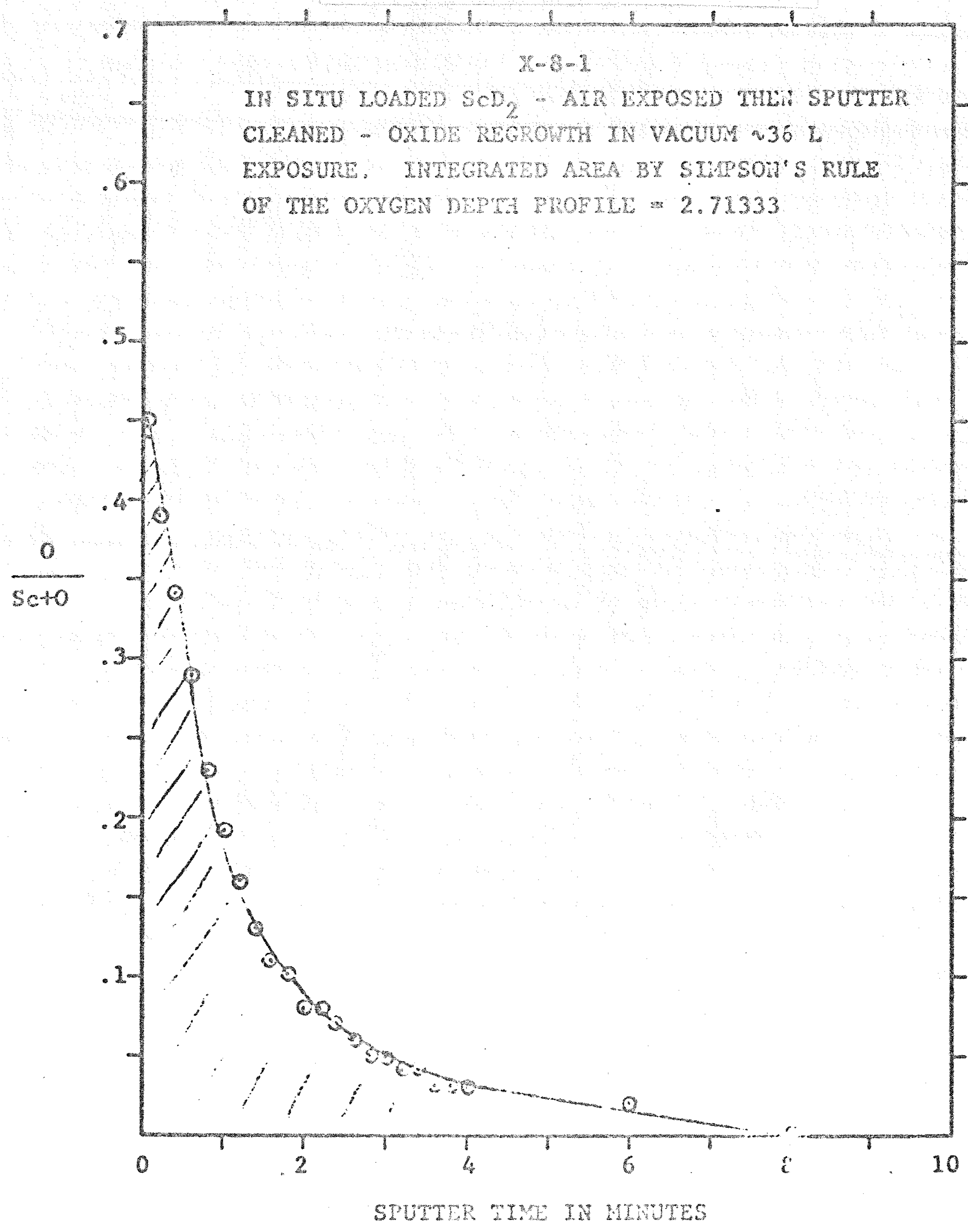

X-8-1
IN SITU LOADED ScD_2 - AIR EXPOSED THEN SPUTTER CLEANED - OXIDE REGROWTH IN VACUUM ∿36 L EXPOSURE. INTEGRATED AREA BY SIMPSON'S RULE OF THE OXYGEN DEPTH PROFILE = 2.71333
.7
.6
.5
.4
.3
.2
.1
O / Sc+O
0
2
4
6
8
10
SPUTTER TIME IN MINUTES

Figure 3

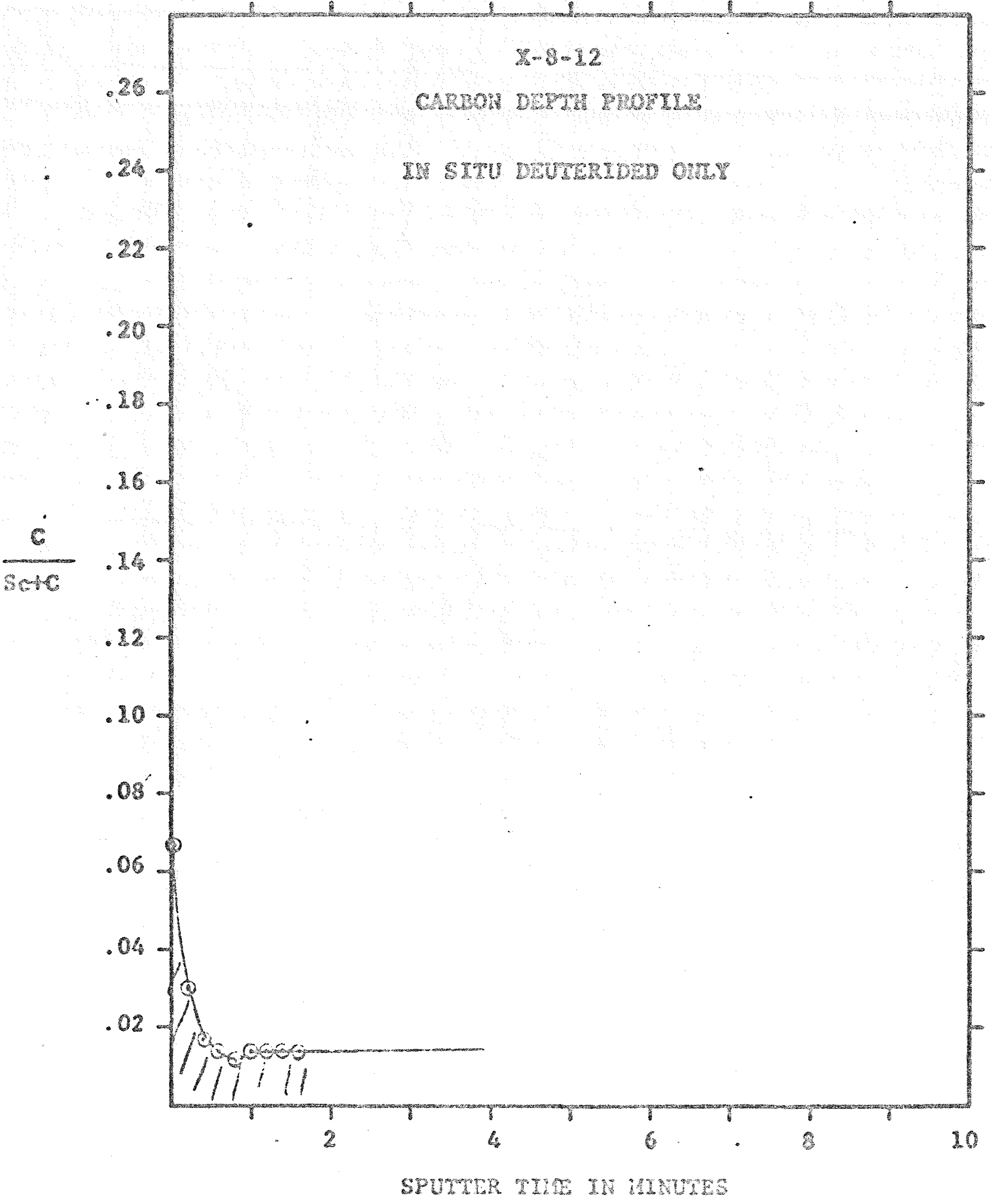

X-8-12
CARBON DEPTH PROFILE
IN SITU DEUTERIDED ONLY
.26
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
C / Sc+C
2
4
6
8
10
SPUTTER TIME IN MINUTES

Figure 4

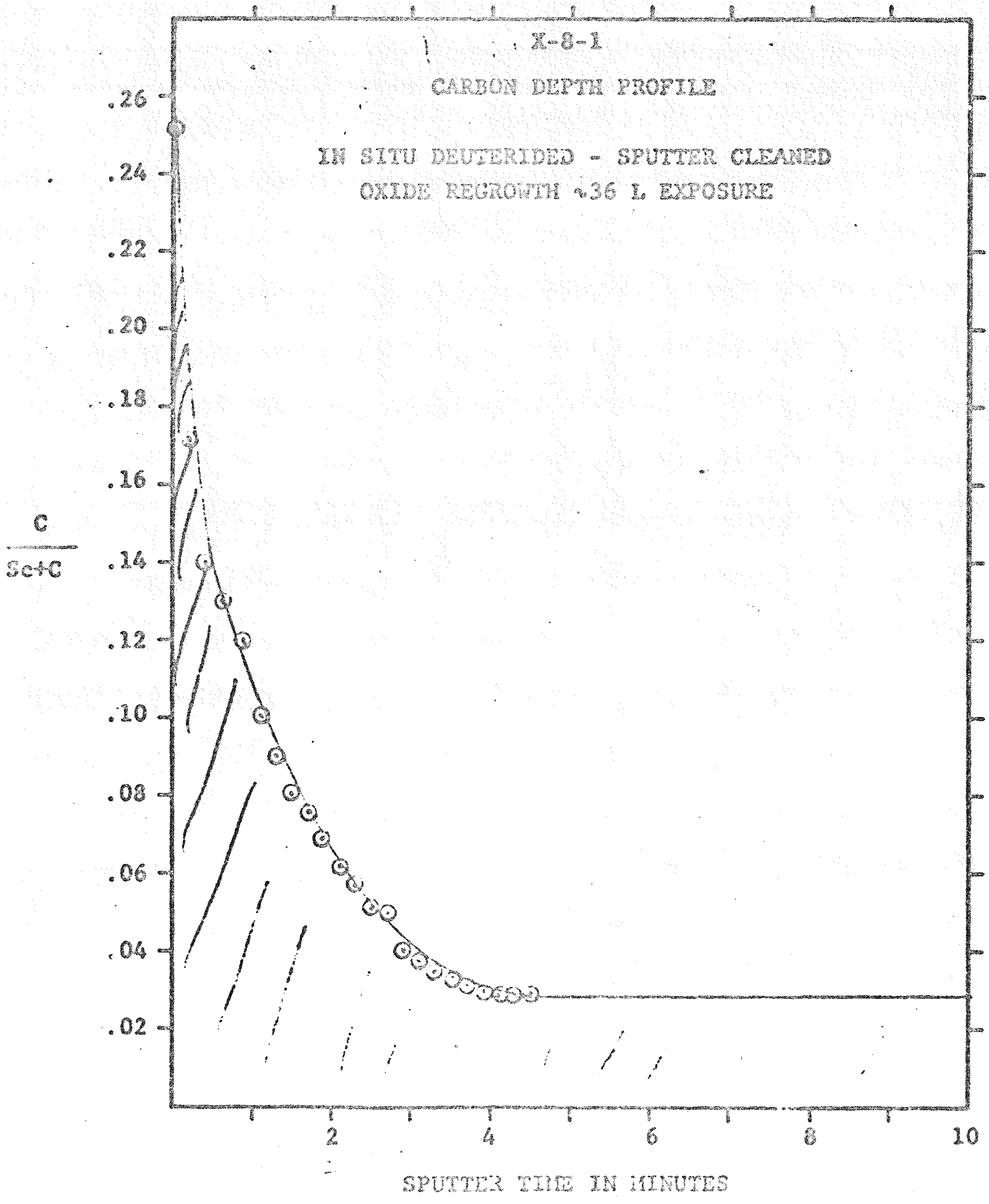
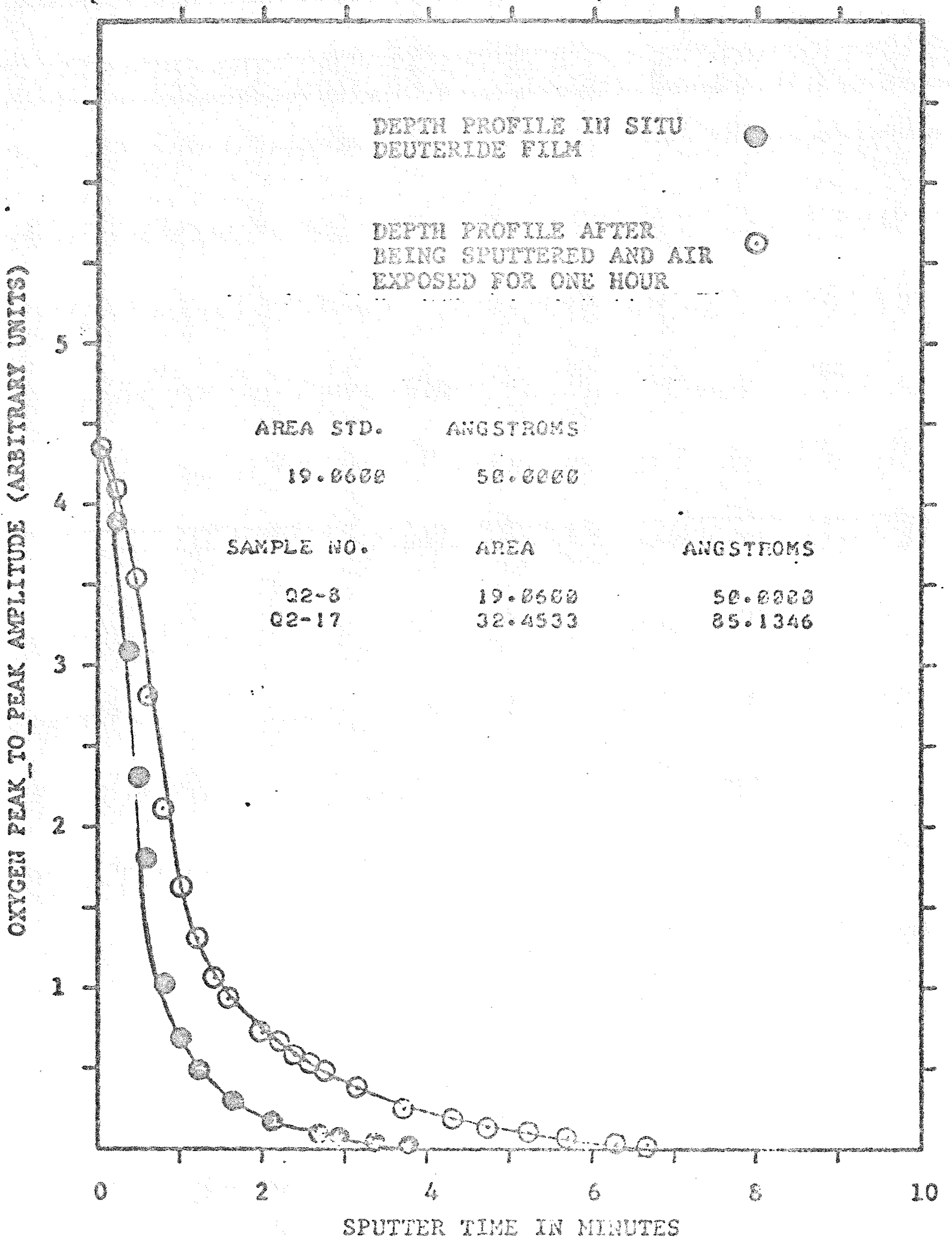

X-8-1
CARBON DEPTH PROFILE
IN SITU DEUTERIDED - SPUTTER CLEANED
OXIDE REGROWTH ~36 L EXPOSURE
C / Sc+C
.26
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
2
4
6
8
10
SPUTTER TIME IN MINUTES

Figure 5



DEPTH PROFILE IN SITU DEUTERIDE FILM ●
DEPTH PROFILE AFTER BEING SPUTTERED AND AIR EXPOSED FOR ONE HOUR ⊙
AREA STD. ANGSTROMS
19.0600 50.0000
SAMPLE NO. AREA ANGSTROMS
02-8 19.0600 50.0000
02-17 32.4533 85.1346
OXYGEN PEAK_TO_PEAK AMPLITUDE (ARBITRARY UNITS)
1
2
3
4
5
0
2
4
6
8
10
SPUTTER TIME IN MINUTES

References

(1) M.F. Berard, C.O. Wirkus, & D.R. Wilder J. Am. Ceram. Soc 51, [11] 643, [1968]

$$x = \left(\frac{2DC_0t}{A\rho}\right)^{\frac{1}{2}}$$ From Crank 111-118

x = movement of the oxide boundary ~cm
D = Diffusivity cm²/sec
t = time sec
C_0 = concentration gradient of the diffusing species gm/cm³
A = difference in mass fraction of the diffusing component and reduced component
ρ = density of oxidized compound gm/cm³

(2) From Data of Harris, Holloway, Bosepflug (Kinetic Data)

$\ln O/\sqrt{t}$ vs $\frac{1}{T}$

$$O = k\sqrt{t}\, e^{-Q/kT}$$

$Q = 0.54\,eV$

$k_1 = 1.14 \times 10^{20}$ Atom/cm²-min$^{\frac{1}{2}}$ or 1.47×10^{19} Atom/cm²/sec$^{\frac{1}{2}}$

$\therefore \quad x = k\, k_1 \sqrt{t}\, e^{-\frac{Q_a}{kT}}$

(*) k_1 = must be converted into gm/cm²-sec
k = cm³/gm However this number will be based on the fact that oxygen density at oxide metal interface is not a bulk pure oxide density value rather, it is

relative density of oxygen in the metal Bulk film. This number is 1.2 to 1.8% by weight.

$$x = \left[\frac{2D_0 e^{-Q_0/kT} C_0 t}{A\rho}\right]^{\frac{1}{2}} \leftarrow x = k k_1 t^{\frac{1}{2}} e^{-Q_R/kT}$$

$$\left[\frac{2D_0 e^{-Q_0/kT} C_0 t}{A\rho}\right]^{\frac{1}{2}} = k k_1 t^{\frac{1}{2}} e^{-Q_R/kT}$$

$$\frac{2D_0 C_0 \cancel{t} \cancel{e^{-Q_0/kT}}}{A\rho} = k^2 k_1^2 \cancel{t} \cancel{e^{-2Q_R/kT}}$$

$$\boxed{D_0 C_0 = \frac{k^2 k_1^2 A\rho}{2}}$$

k for 1.2%

$$D_0 C_0 = \frac{(61.96)^2 (3.768 \times 10^{-4})^2 (.35)(3.864)}{2}$$

$$k = \frac{1}{(3.864)(0.012)} \frac{cm^3}{gm}$$

$$\boxed{D_0 C_0 = 3.69 \times 10^{-4} \frac{gm}{cm\text{-}sec}}$$

TABLE I

IN SITU ErD_2 REACTED AT ~500°C FOR THIRTY MINUTES

SAMPLE No.	P_2	D_2	ADMITTED CO	BACKGROUND CO	H_2/CO	XRD
(1)	1.09	42.52	CONTROL			ErD_2
(2)	4.57	20.16	$1X10^{-5}$		1.12	Er_2O_3 ErD_2
(3)	2.41	4.52	$6X10^{-7}$		.037	Er-S Er_2O_3-W
(4)	2.33	2.40		$6X10^{-7}$	.28	Er-S Er_2O_3-S ErD_2-W
(5)	3.3	.38	$2X10^{-6}$		.04	Er ONLY
(6)	4.5	30.77		$2X10^{-6}$	.43	ErD_2-S Er_2O_3-S

FIGURE 3

THE EFFECT OF OXIDATION REFLECTED

IN THE LOADING RATIO VERSUS AREAL DENSITY

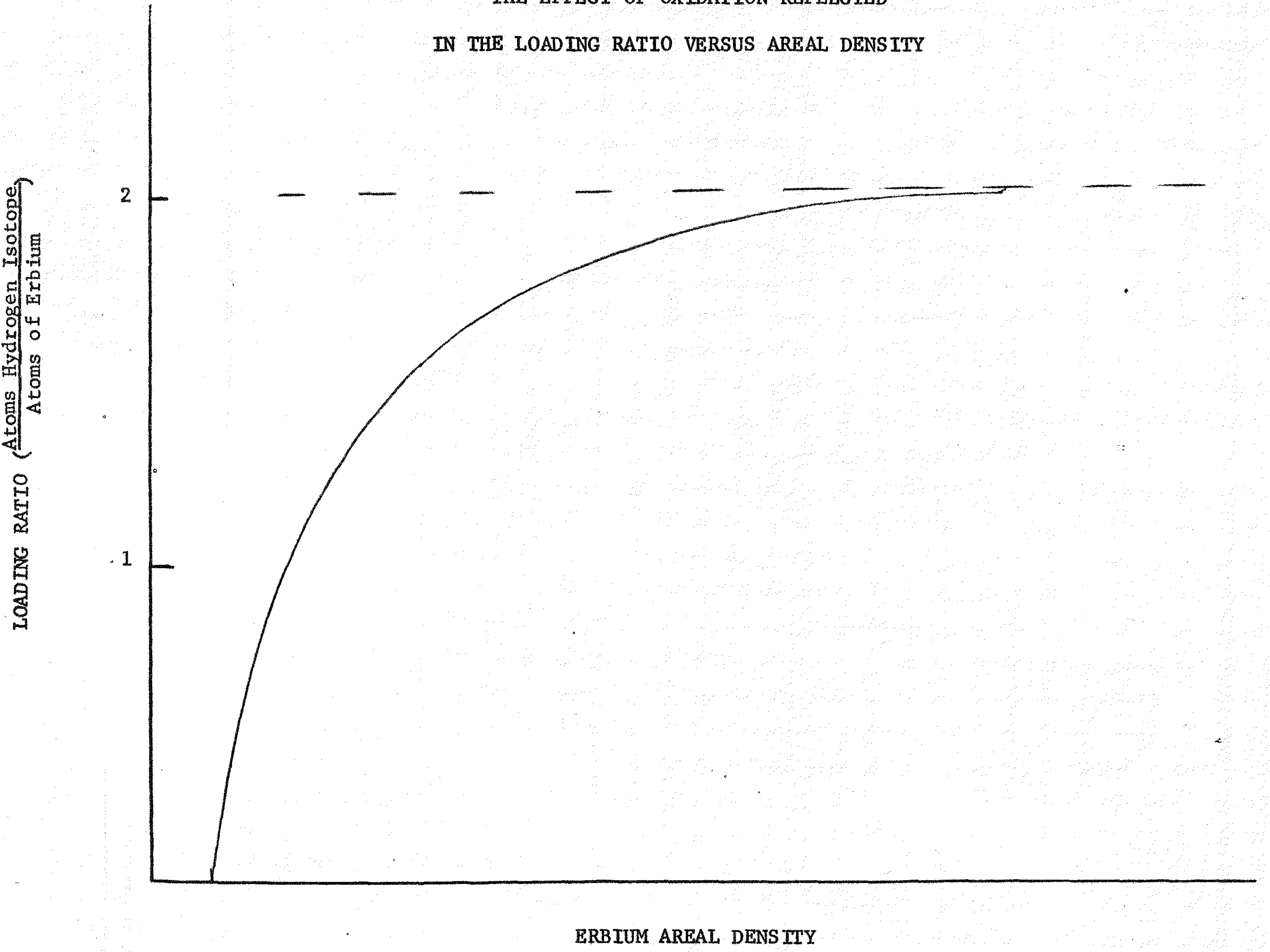


FIGURE 4

ERBIUM METAL UNAVAILABLE FOR HYDRIDING BEFORE & AFTER THERMAL VACUUM ANNEAL

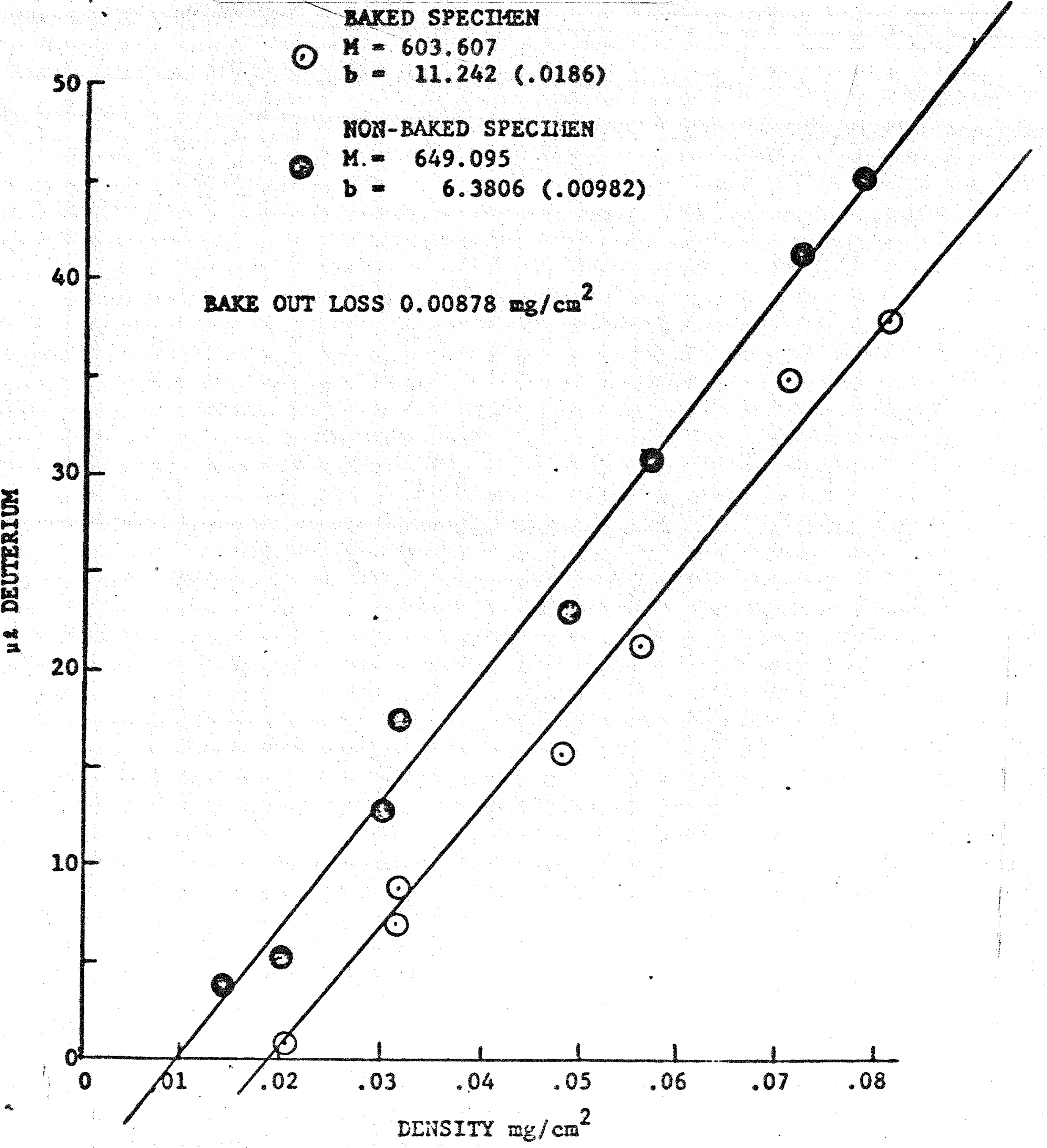


FIGURE 5

CO GROWTH ON SPUTTER CLEANED ErD_2 AT ROOM TEMPERATURE

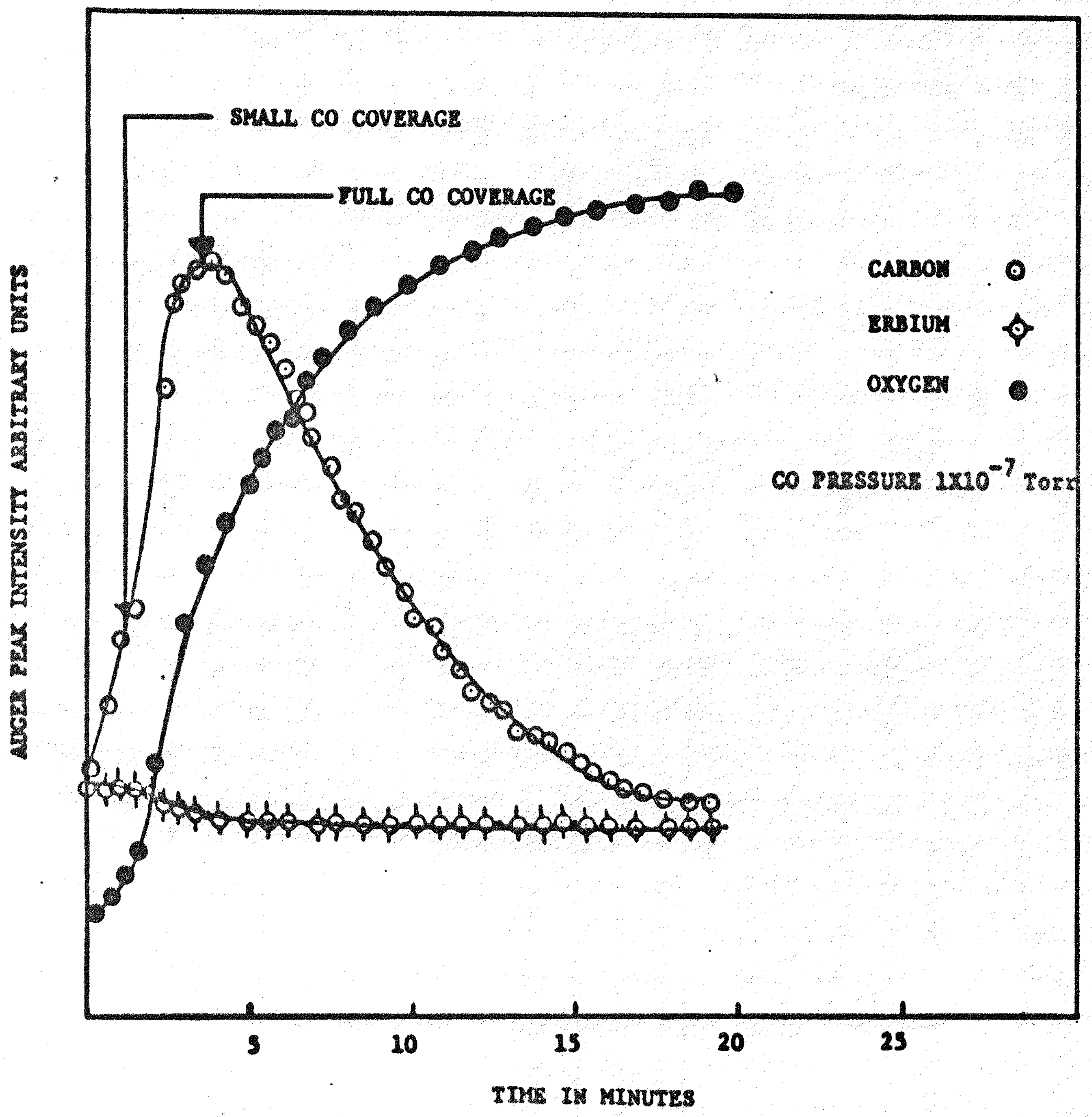
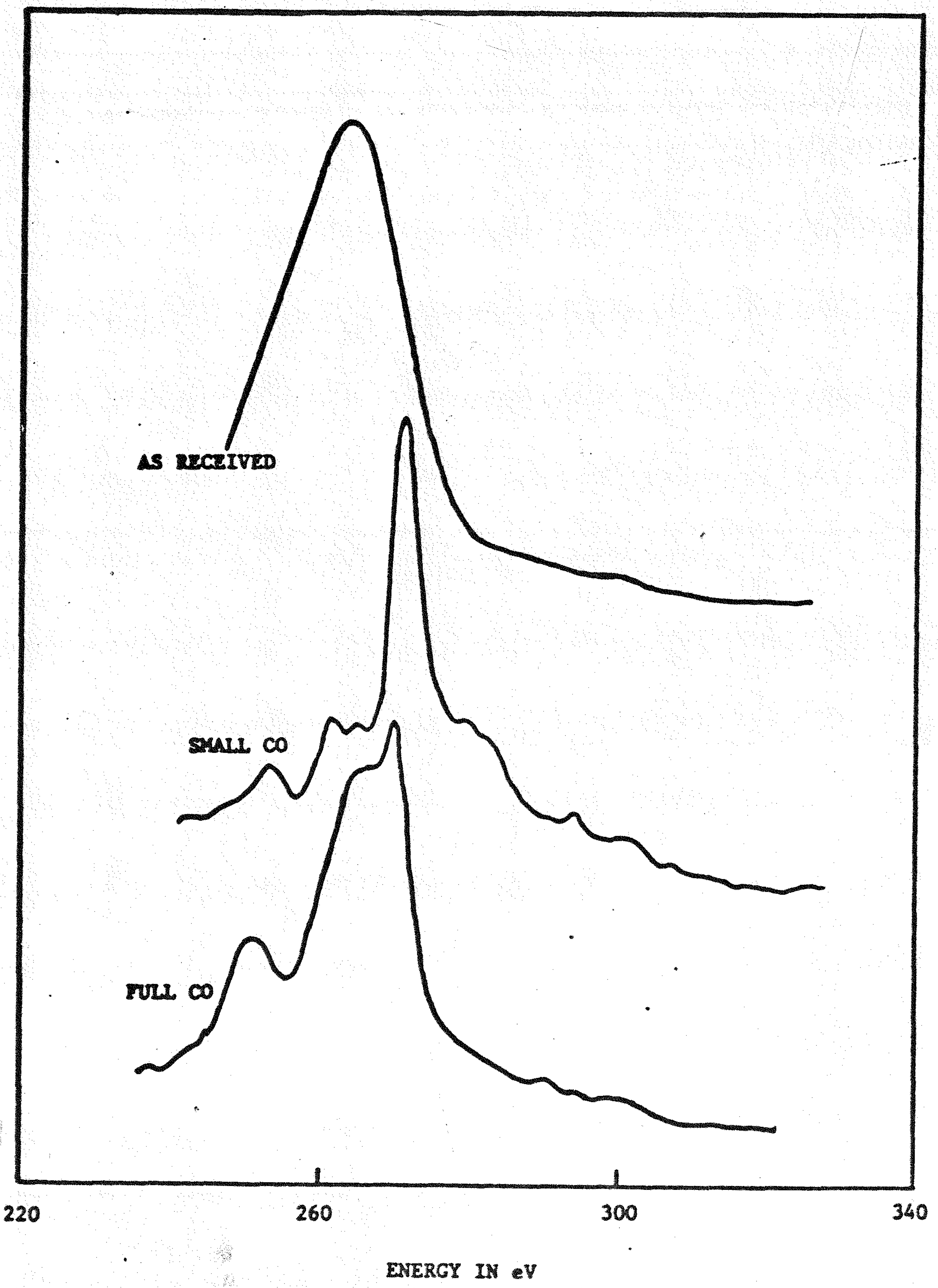


FIGURE 6

CARBON AUGER SPECTRUM AT DIFFERENT COVERAGES OF CO ON SPUTTER CLEANED ErD_2



ERBIUM AUGER SPECTRUM AT DIFFERENT COVERAGES OF CO ON SPUTTER CLEANED ErD_2

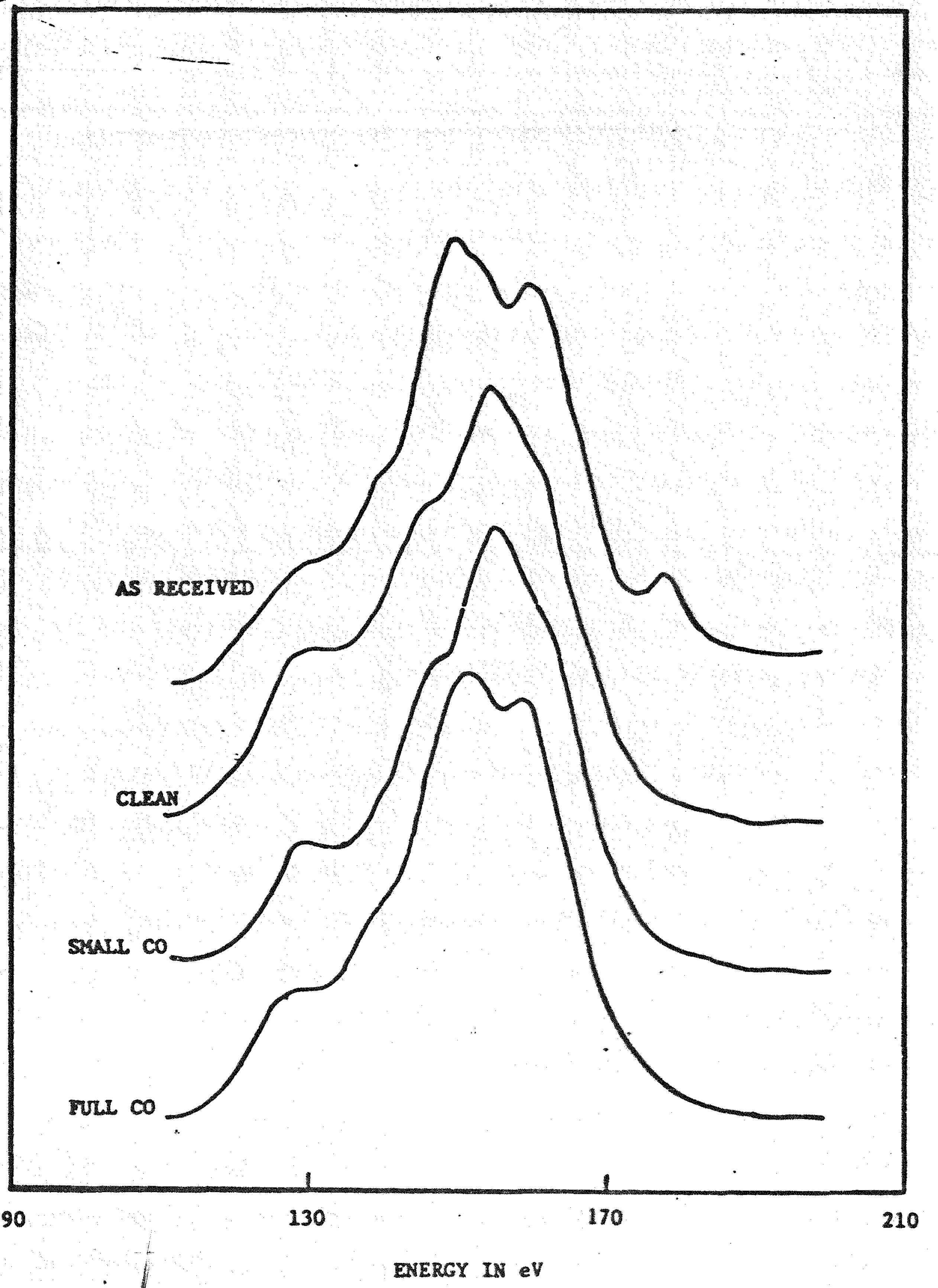


FIGURE 8

OXYGEN AUGER SPECTRUM AT DIFFERENT COVERAGES OF CO ON SPUTTER CLEANED ErD_2

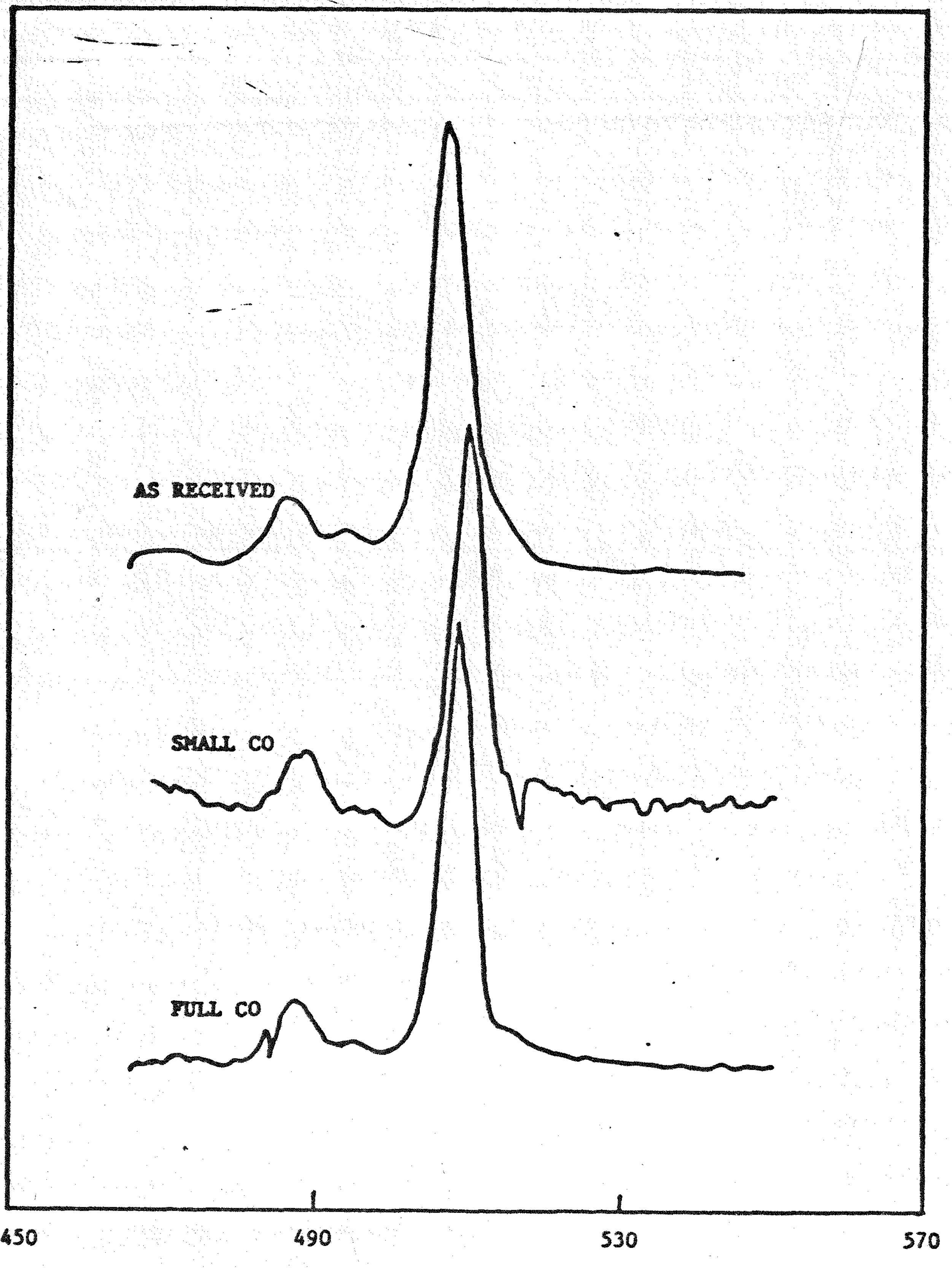


TABLE 2

ScD_2 INTERACTION WITH CO

USING RADIANT HEATER

IN SITU ScD_2 REACTED ~500°C FOR 1/2 HOUR

SAMPLE #	P_2 μℓ	D_2 μℓ	ADMITTED CO	BACKGROUND CO	XRD
1 CONTROL	3.75	450.81	NOT REACTED		ScD_2
2	6.26	215.19	5×10^{-6}		Sc METAL
3	.54	.97		5×10^{-9}	Sc METAL
4	-	-	1.7×10^{-5}		Sc_2O_3

TABLE 3

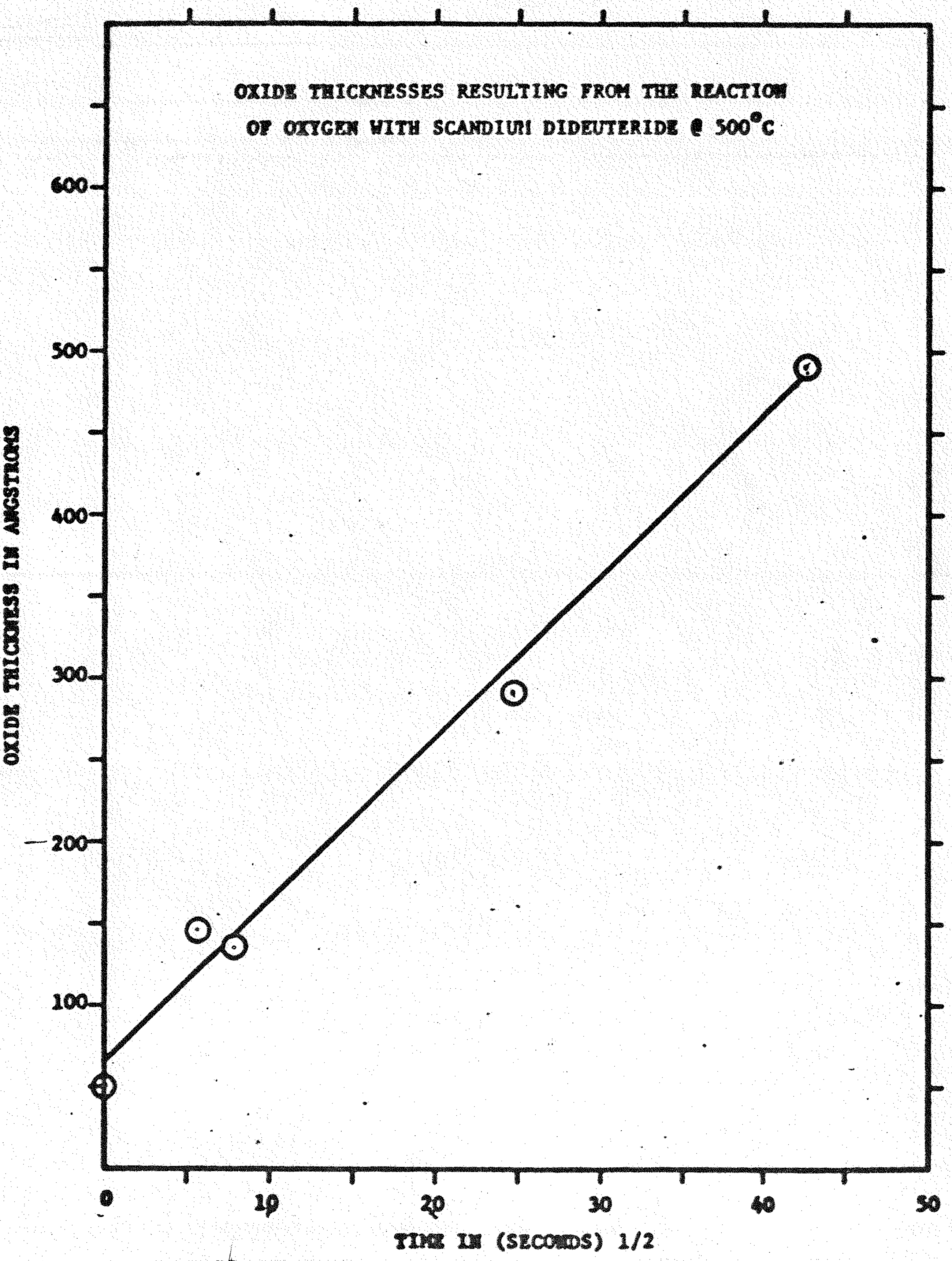
ScD_2 INTERACTION WITH CO

USING INDIRECT HEATER

SAMPLE No.	GAS ANALYSIS P_2(μℓ)	 D_2(μℓ)	X-RAY ANALYSIS	REACTION TEMP. (°C)	REACTION PRESS (Torr)
Q2-12	2.04	63.17	ScD_2	-	-
Q2-5	2.30	63.72	ScD_2	500	$1X10^{-8}$
Q2-11	2.13	65.17	ScD_2	500	$1X10^{-8}$
Q2-7			ScD_2	500	$1X10^{-8}$
Q2-20			ScD_2	-	-
Q2-1			ScD_2	500	$>3X10^{-7}$
Q2-18	1.3	6.13	Sc	500(f)	$5X10^{-7}$
Q2-15	2.18	7.78	Sc	500(f)	$5X10^{-6}$

(7-1-74)

FIGURE 12



OXIDE THICKNESSES RESULTING FROM THE REACTION OF OXYGEN WITH SCANDIUM DIDEUTERIDE @ 500°C

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