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AES AND XPS STUDY OF PLUTONIUM OXIDATION*

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The initial oxidation of plutonium metal at 27 °C has been studied using AES and XPS. Initially a "clean" plutonium surface was prepared by Ar^+ bombardment and 500 °C-Ar^+ bombardment heat cycles. Changes occurring in the plutonium Auger electron spectra in the energy range of 40 to 120 eV and the $4f_{5/2}$, $4f_{7/2}$ (core levels), and 5f, 7s (valence band) XPS peaks were monitored during oxygen exposure (10 to 1.8 X 10^8 L). Examination of the $4f_{7/2}$ level revealed two oxidation states which are attributed to a suboxide and PuO_2. The $4f_{7/2}$ binding energies for the two oxidation states and plutonium metal are 426.1, 424.4, and 422.2 eV, respectively. By taking the Auger ratio [O(511 eV)/Pu(317 eV)], it was observed that oxidation proceeded by two steps. In the first step there was a rapid increase of oxygen with the formation of the suboxide. In the second stage, the O(511 eV)/Pu(317 eV) ratio was constant with conversion of the suboxide to PuO_2.

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DISCLAIMER

INTRODUCTION

Until recently, there have been very few studies of gas reactions with the actinides using surface techniques.[1] Most of the current surface studies have involved thorium and uranium.[2-8] Little work has been done on plutonium because more sophisticated facilities are necessary to safely handle plutonium and protect the environment because of its alpha emission and toxicity. Also only a few laboratories have access to plutonium. The few surface studies that have been made on plutonium are kinetic studies on the formation of thin oxide films using ellipsometry[9,10] and adsorption studies by dynamic pumping measurements.[11]

Auger electron spectra have been taken on plutonium,[12] but a surface free of oxygen could not be obtained with the experimental method of in situ scrapping. There was no provision for cleaning the specimen with Ar^+ bombardment or in situ heating.

The oxides and carbides of plutonium are stable compounds and difficult to remove from the metal. For instance, the heat of formation of PuO_2 at 300 K is -252.9 kcal/mol.[13] Possible oxides that could exist on the surface are PuO, Pu_2O_3(β-Pu_2O_3), $PuO_{1.52}$ (α-Pu_2O_3), and PuO_2. These oxides are semiconductors and their type is dependent on stoichiometry and preparation conditions. For example, $Pu_{2.00}$ is p-type while PuO_{2-x} (x = 1.97 to 1.99) with oxygen vacancies is n-type.[1]

In this study, a relatively clean surface was prepared by Ar^+ bombardment and in situ heat treatments. Then Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to examine the surface

after oxygen exposure. Reported here are AES changes which occurred in the energy range of 40 to 120 eV and XPS changes in the $4f_{5/2}$, $4f_{7/2}$ (core), and 5f, 7s (valence band) levels. The oxidation reaction was followed for oxygen exposures of 10 to 1.8×10^8 L [1L(Langmuir) = 1×10^{-6} Torr sec] at 27 °C.

EXPERIMENTAL

The plutonium specimen used in this investigation was from a double electro-refined batch. The major impurities were: Am - 522, Ga - 107, Fe - 99, Cr - 76, Al - 64, Ta - 60, Ni - 38, Zn - 28, C - 23, and Si - 22 ppm. The surface of the specimen was prepared by abrasion with 360 grit silicon carbide paper and rinsed with 1,1,1 trichloroethane. Then the sample was transferred to the glovebox which completely encloses the vacuum chamber. The plutonium was placed between two 0.254 mm thick tantulum sheets on the sample holder. The outer sheet had a 5 mm diameter hole cut out which exposed the plutonium surface. An alumel-chromel thermocouple was spot welded to the back side of the outer tantalum sheet. With this arrangement, temperature measurements near 500 °C were within 50 °C.

After evacuation of the chamber, a vacuum bakeout at 220 °C for 72 hours reduced the pressure to 120 nPa (1 Pa = 7.52×10^{-3} Torr). The plutonium oxide and other impurities (carbon, chlorine, and sulfur) were removed by 1 keV ($\sim$130 $\mu A/cm^2$) Ar^+ bombardment. At this bombardment condition, the removal rate determined by ellipsometric measurements for a UO_2 film on uranium is about 16 Å/min. Using this sputter etch rate, about 2 μm were removed from the plutonium surface.

For further cleaning, the specimen was heated at 500 °C for 30 min. The heat treatment caused a large amount of chlorine to segregate to the surface. Also plutonium carbide was formed probably from a reaction with the residual gases (CO-500 nPa, CO_2-200 nPa) during the heat treatment. These surface constituents were removed by taking 500 Å off the surface with Ar^+ bombardment. This 500 °C heat and Ar^+ bombardment cycle was repeated 25 times. After this treatment, a relatively "clean" surface was obtained.

The surface was examined with AES and XPS using a double pass cylindrical mirror analyzer.[14] The X-ray source for XPS was Mg kα with an energy of 1253.6 eV. The calibration of the spectrometer was checked using the Auger electron peaks of 69 and 2024 eV for gold and the Au $4f_{7/2}$ peak at 83.8 eV. The Pu 4f peaks were recorded with a resolution of 0.5 eV while the resolution for Pu 5f, 7s and O 1s was 1 eV.

AES showed only carbon (in carbide structure) and oxygen impurities on the surface after cleaning. The Auger electron peak-to-peak height ratios were C(272 eV)/Pu(317 eV) = 0.47 and O(511 eV)/Pu(317 eV) = 0.22. Although AES did not show any tantalum on the surface, XPS showed some tantalum contamination with a Ta($4d_{5/2}$)/Pu($4f_{7/2}$) peak ratio of 0.04. The tantalum was propably sputtered off the tantalum holder onto the plutonium surface.

After preparation of this "clean" surface, oxygen was admitted with the specimen at 27 °C, and spectra were recorded after each exposure. The oxygen pressures ranged from 13.3 μPa to 1.33 Pa. During exposure except at 1.33 Pa, a dynamic oxygen flow was maintained to keep the oxygen

reasonably pure. At 1.33 Pa oxygen exposure, the system was static. A partial pressure analysis at 133 μPa showed that the amount of CO in the gas was about 4%.

RESULTS AND DISCUSSION

A. AES CHANGES AFTER OXYGEN EXPOSURE

Changes in the plutonium Auger electron spectra and increases in the oxygen peak upon oxygen exposure are shown in Figure 1. To enhance the spectra in the 40 to 120 eV range, a negative 50 V bias was put on the sample. The most notable change in the spectra is the shift of the 97 eV peak to 91 eV after oxygen exposure.

Energies of the Auger transitions observed experimentally and calculated for plutonium and PuO_2 are listed in Table I. Transition energies were calculated from the relation[15] $E = E_W - E_X - E_y$ for a (WXY) Auger electron transition.

The previous correlation of experimental Auger electron transitions with calculated values[12] are in error when the P_1, P_2, and/or P_3 levels are involved. Recent results of Veal et al[16] for PuO_2 show that incorrect values for the P levels were used. In these calculations, the values used for the energy levels are our XPS results and are given in Table II. To correct for the work function of the analyzer and the fact that the experimental energy is the minimum of the derivative $(\frac{dN(E)}{dE})$ and the calculated energy is for the midpoint of the derivative (N(E)-peak maximum), the chlorine ($L_3M_{2,3}M_{2,3}$) minimum determined experimentally at 180 eV was compared to 181 eV calculated by Coghlan and Clausing.[18] Thus, 1 eV was

subtracted from the calculated energies. The calculated energies are in reasonable agreement with experimental Auger electron peaks. Also the peak structure and Auger transition designation of the other actinides, uranium[7] and thorium,[3] are quite similar.

B. XPS CHANGES IN $4f_{5/2}$, $4f_{7/2}$, AND VALENCE BAND

Changes occurring in the 4f plutonium peaks after oxygen exposure are presented in Figure 2. These spectra revealed two oxidation states with the first state being attributed to a plutonium suboxide and the second to PuO_2. No peak shifts were observed for O 1s measured at 530.0 eV.

Also changes in the valence (5f, 7s) band were monitored during oxygen exposures. The O 2p peak was not resolved in the valence band. Also two distinct oxidation states were not observed as they were for the 4f core levels. As oxidation proceeded the 5f, 7s level shifted to higher binding energies. Observation of the 5f,7s peak widths (FWHM) in relation to changes occurring in the 4f peaks shows that the peak broadens when more than one chemical state is present. The energies of the 4f and 5f, 7s levels and the 5f, 7s FWHM after oxygen exposures are presented in Table III.

OXIDATION PROCESS

By taking the Auger peak-to-peak height ratio [O(511 eV)/Pu(317 eV)] it was observed that oxidation proceeded by two steps (Figure 3). In the first step, there was a rapid increase of oxygen with the formation of the suboxide as shown by XPS. In the second stage, the O(511 eV)/Pu(317 eV) ratio was constant with conversion of the suboxide to PuO_2. Based on ellipsometric data,[9] the total oxide thickness after 1.8×10^8 L oxygen

would be about 200 Å.

The oxygen uptake as a function of oxygen exposure obtained from Auger data is similar to data obtained by Adams and DiGiallonardo[11] for the adsorption of oxygen on plutonium at 300K. These data were obtained by dynamic pumping measurements, and the lower curve in Figure 3 shows the results.

A further comparison with the adsorption data can be made at 10 L oxygen exposure. The thickness of the suboxide film can be determined from the XPS $4f_{7/2}$ peaks by using the equation[19] $I_S = I_{OS} \exp(-x/0.75\mu)$ where:

I_S = signal of substrate,

I_{OS} = signal of pure substrate,

x = thickness of surface film, and

μ = electron mean free path.

The electron mean free path can be determined from $\mu = 0.5\sqrt{E}$ Å[20] where E is the kinetic energy in electron volts. This calculation gives a thickness of 5.9 Å which is in reasonable agreement with 2.5 Å determined from the adsorption data of Adams and DiGiallonardo.[11]

SUMMARY

Examination of the oxygen-plutonium reaction at 27 °C and oxygen exposures from 10 to 1.8×10^8 L by AES and XPS showed that the oxidation involved two steps. During the initial oxygen exposure or chemisorption phase, there was a rapid increase in oxygen on the surface. Oxidation caused an increase of 2.2 eV in the binding energy of the Pu $4f_{7/2}$ electrons,

and this oxidation state is considered to be a suboxide.

After the chemisorption phase, the second oxidation stage would involve the diffusion of oxygen anions to the plutonium metal interface. Monitoring oxygen uptake on the surface with AES showed no further increase. A new oxidation state appeared in which the $4f_{7/2}$ binding energy was increased by 3.9 eV from "clean" plutonium. This oxide is probably PuO_2. During this second stage, the suboxide was converted to PuO_2.

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Table I. Plutonium Auger electron transitions.

Transition	Pu		PuO_2	
	E_{CALC}(eV)	E_{OBS}(eV)	E_{CALC}(eV)	E_{OBS}(eV)
$O_4P_2P_2$	45		47	
$O_4P_1P_3$	51	50	51	49
$O_5P_2P_3$	52		53	
O_5P_1V	55		53	
$O_4P_2P_3$	62	61	63	
O_4P_1V	64		62	
O_5P_2V	66		64	64
$O_5P_3P_3$	69	68	68	
O_4P_2V*	75		74	
$O_4P_3P_3$	79	80	78	79
O_5P_3V*	83		80	
O_4P_3V	93		90	
O_5VV*	96	97	92	91
O_4VV*	106	103	101	103
		109		112

* Transitions used to designate experimentally observed Auger electron peaks for uranium[7] and thorium.[3]

Table II. Energy levels of plutonium.

Energy Level		Pu Binding Energy (eV)	PuO_2 Binding Energy (eV)
O_4	$(5d_{3/2})$	111.3*	114.4*
O_5	$(5d_{5/2})$	101.5	104.6
P_1	(6s)	43.8	45.0
P_2	$(6p_{1/2})$	32.8	33.2
P_3	$(6p_{3/2})$	15.5	17.6
$V \equiv O_{6,7}, Q_1$	(5f,7s)	2**	6**

* Estimated from energy separation between j subshells in atoms given by Carlson.[17]

** Bonding bands of uranium[7] used as approximations for plutonium.

Table III. Binding energies of Pu $4f_{5/2}$, $4f_{7/2}$ and 5f,7s electrons and FWHM of 5f,7s peak during oxidation.

Oxygen Exposure (L)	$4f_{5/2}$(eV)			$4f_{7/2}$(eV)			5f,7s(eV)	5f,7s FWHM (eV)
	PuO_2	Suboxide	Pu	PuO_2	Suboxide	Pu		
CLEAN		436.7(S)	434.9		423.6(S)	422.2	0.1	3.0
10		436.5	435.0(S)		424.3	422.4(S)	0.5	3.6
160		437.1			424.4		1.2	3.0
500		437.1			424.3		1.3	3.2
$5X10^3$		437.2			424.5		1.5	3.3
$5X10^4$	438.4	437.0(S)		426.1	424.5(S)		1.9	3.6
$5X10^5$	438.4	437.2(S)		425.9	424.4(S)		2.0	3.8
$5X10^6$	439.0	437.0(S)		426.1	424.6(S)		2.1	3.6
$4.25X10^7$	438.7			426.0	424.4(S)		2.3	3.3
$1.8X10^8$	438.7			426.1	424.0(S)		2.3	3.3

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FIGURE CAPTIONS

Figure 1. AES changes after exposure of plutonium to oxygen.

Figure 2. XPS changes in 4f peaks after exposure of plutonium to oxygen.

Figure 3. Increase of oxygen on plutonium surface measured by Auger peak-to-peak height ratio [O(511 eV)/Pu(317 eV)]. Lower curve shows the oxygen adsorption data of Adams and DiGiallonardo.[11]

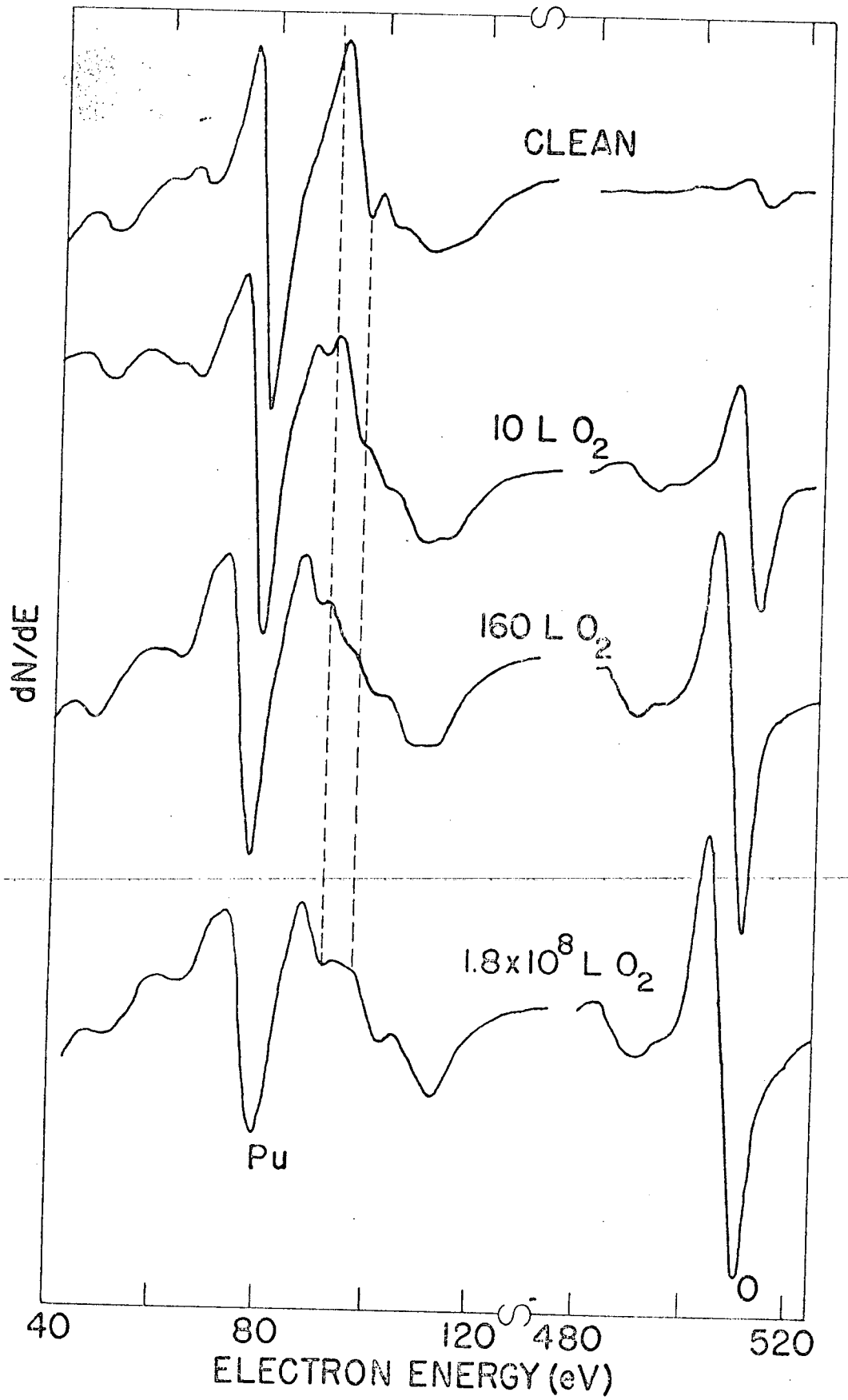
CLEAN
10 L O2
160 L O2
1.8x10^8 L O2
dN/dE
Pu
O
40
80
120
480
520
ELECTRON ENERGY (eV)

Figure 1

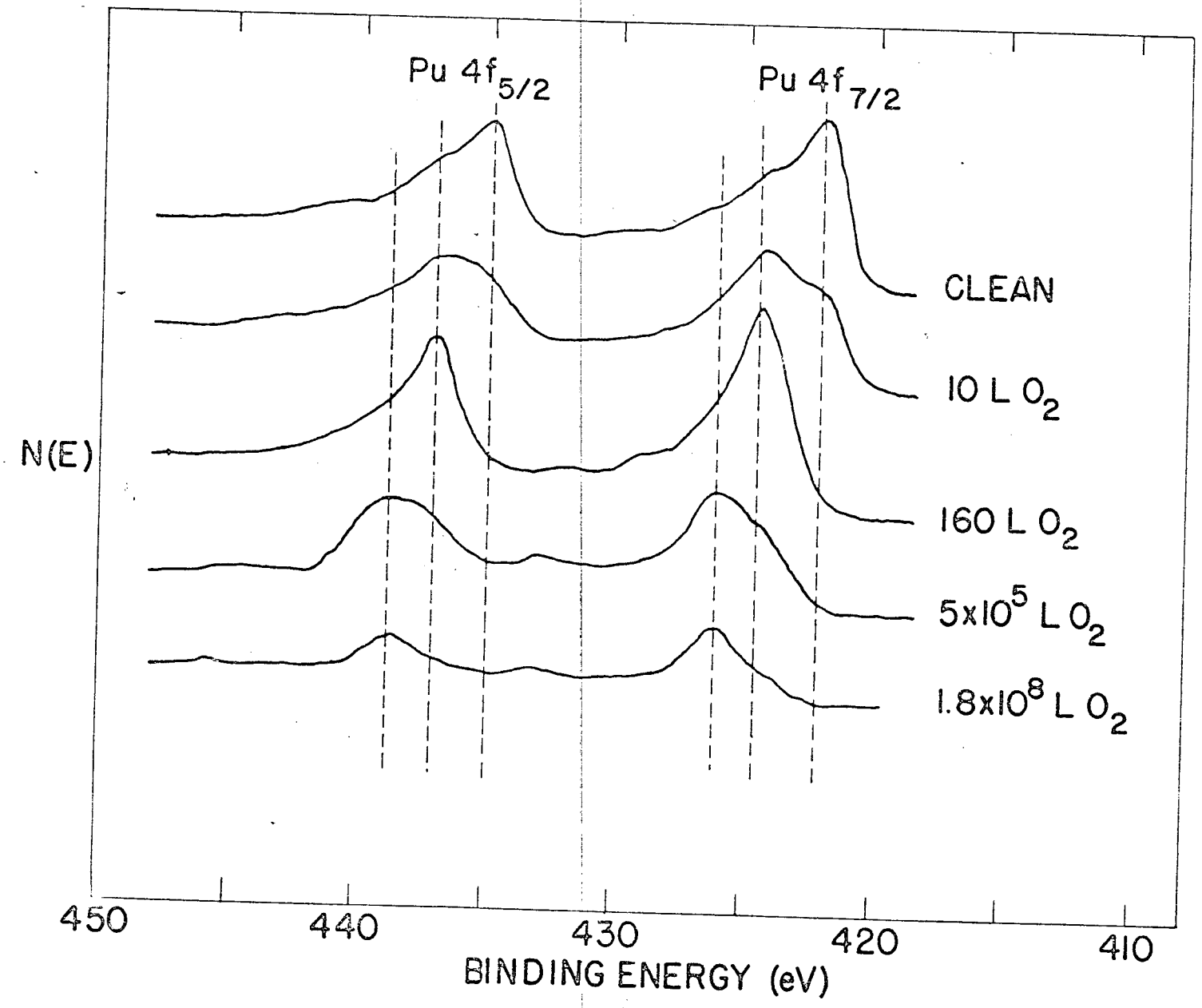
Pu 4f5/2
Pu 4f7/2
CLEAN
10 L O2
160 L O2
5x10^5 L O2
1.8x10^8 L O2
N(E)
450
440
430
420
410
BINDING ENERGY (eV)

Figure 2

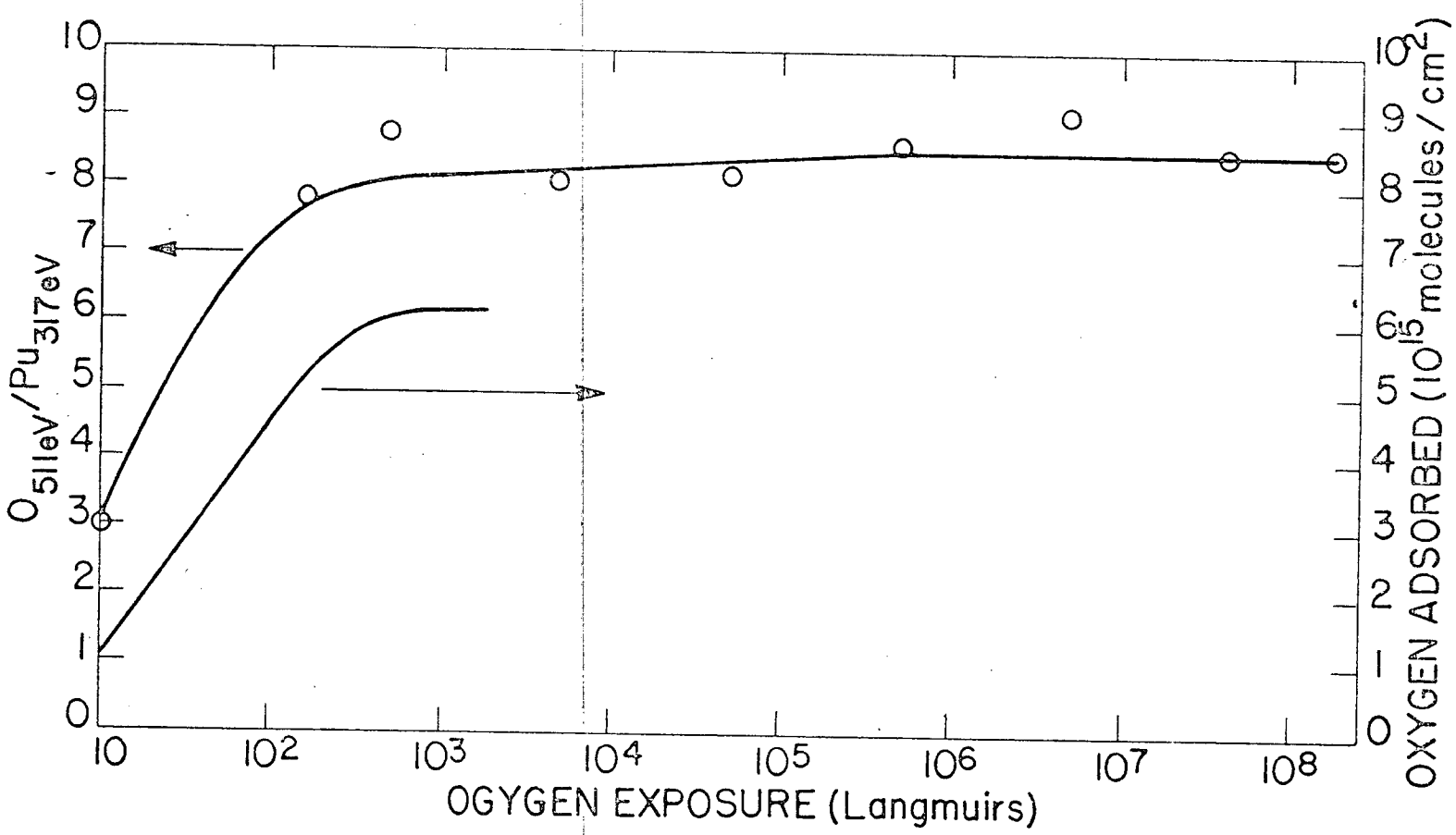
O_{511eV}/Pu_{317eV}
OXYGEN ADSORBED (10^{15} molecules/cm^2)
OGYGEN EXPOSURE (Langmuirs)
0
1
2
3
4
5
6
7
8
9
10
10^2
10^3
10^4
10^5
10^6
10^7
10^8

Figure 3.