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EFFECT OF VACUUM HEAT TREATMENT ON PLUTONIUM OXIDE SURFACES AS STUDIED BY XPS AND AES

MASTER

D. T. Larson

ABSTRACT

The effect of heating (150 to 500°C) in vacuum a plutonium substrate with a plutonium oxide surface film was studied utilizing X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). When plutonium metal with a surface oxide film is vacuum heat treated, the oxide is reduced by reaction of the substrate metal with the oxide. The reactions occurring were examined by monitoring the binding energies of the Pu($4f_{7/2}$), O(1s), and C(1s) XPS peaks and observing the C(KLL) Auger electron peak structure. These results were compared with the X-ray diffraction data of Terada et al.[1] The XPS and AES data show that at higher reaction temperatures (400-500°C) the surface compound formed is not PuO as indicated by Terada et al but is instead a plutonium oxycarbide (Pu[C,O]) compound. The Pu ($4f_{7/2}$) binding energies for PuO_2, $PuO_{1.52}$ (α-Pu_2O_3), Pu(C,O), and Pu metal are 426.1, 424.4, 423.6, and 422.2 eV, respectively.

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INTRODUCTION

When plutonium metal with a surface oxide film is vacuum heat treated the oxide is reduced by reaction of the substrate metal with the oxide. Previously Terada et al[1] studied these reactions by X-ray diffraction. They observed the reactions with the calculated free energy changes

		ΔG(kcal)	Temp (°C)
(1)	$Pu + 3\ PuO_2 \rightarrow 2\alpha\text{-}Pu_2O_3$	-105	200
(2)	$Pu + \alpha\text{-}Pu_2O_3 \rightarrow 3\ PuO$	+ 26	400

The positive free energy change of reaction (2) indicates that this reaction should not take place. Terada et al[1] suggested that the reaction occurs because the surface film energies stabilize this oxide.

Another possibility is that PuO is not the compound formed, but the compound is instead plutonium oxycarbide. Mulford et al[2] in their work on the plutonium-carbon-oxygen system show a Pu(C,O) phase. The stoiciometry of an oxygen rich compound would be $PuC_{0.35}O_{0.65}$. With the same lattice constant and crystal structure, X-ray diffraction would be unable to distinguish between plutonium oxycarbide and plutonium monoxide.

To examine this reaction in greater detail, the vacuum heat treatment of plutonium with a surface oxide film was examined utilizing the surface techniques X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). With these surface techniques,[3,4] the surface elements can be determined and the XPS peak shifts can give information on the chemical state of the surface. Thus, it should be possible to ascertain whether or not reaction (2) yields plutonium monoxide or plutonium oxycarbide. Also a comparison of data obtained by the surface spectroscopic techniques XPS and AES with the X-ray diffraction data of Terada et al[1] will be informative.

This will allow a correlation of oxide type with binding energy shifts observed for the XPS Pu ($4f_{7/2}$) peak.

EXPERIMENTAL

The plutonium specimen, sample holder, and AES-XPS system were the same as reported in an earlier study on the oxygen-plutonium reaction at ambient temperature.[5] The preparation of the plutonium specimen consisted of (1) abrading with 360 grit silicon carbide paper, (2) rinsing with 1,1,1 trichloroethane, (3) placing in AES-XPS vacuum chamber, (4) evacuating to 120 nPa, (5) preparing a "clean" surface by Ar^+ bombardment and 500°C heat treatments, and (6) forming ∿200 Å PuO_2 film by exposure to 1.8×10^8 L oxygen.

This specimen was then given in situ vacuum heat treatments. The sample was heated by electron bombardment. The plutonium was sandwiched between two 0.254 mm thick tantalum sheets. The outer sheet had a 5 mm diameter hole which exposed the plutonium surface. Temperature measurements were made with a chromel-alumel thermocouple which was spot welded to the back side of the outer tantalum sheet. With this arrangement temperature measurements near 500°C were accurate within 50°C. During the heat treatments, typical vacuum conditions at 150°C were CO-0.3μPa, CO_2-0.1μPa, H_2O-0.2μPa with the total pressure being ∿0.7μPa and at 500°C were CO-2μPa, CO_2-1μPa with the total pressure being ∿4μPa.

After heating, the surface was examined with AES and XPS using a double pass cylindrical mirror analyzer.[6] The X-ray source for XPS was Mgkα with an energy of 1253.6 eV. The calibration for XPS was checked using the Au($4f_{7/2}$) peak at 83.8 eV.

RESULTS AND DISCUSSION

Changes occurring in the XPS Pu($4f_{7/2}$) peak after vacuum heat treatments are shown in Figure 1. Heating the oxide (PuO_2), formed at ambient temperature, at 150°C produces a shift in the XPS Pu($4f_{7/2}$) peak. The X-ray diffraction data of Terada et al[1] show that the oxide formed at these conditions is $PuO_{1.52}$(α-Pu_2O_3). Further heat treatments at higher temperatures (500°C) indicates that another Pu$4f_{7/2}$ peak shift occurs. There is also an increase in the peak width (FWHM). At 300°C, the FWHM is 3.3 eV while at 500°C, the FWHM is 3.8 eV (See Table I). These changes indicate that the state of the oxide has changed.

Examination of the effect of temperature on the C(1s) peak reveals that a change in the carbon state starts to appear at 400°C (See Figure 2). The peak at 284.6 eV is attributed to a hydrocarbon while that at the lower binding energy of 281.0 eV to a plutonium carbide type. The AES spectra of carbon presented in Figure 3 also shows this change in the state of carbon beginning at 400°C. This simultaneous change in the oxide and carbon states suggests that the high temperature reduction produces a plutonium oxycarbide compound.

The amount of oxygen relative to plutonium for each treatment was determined both from the AES and XPS spectra. The oxygen, plutonium ratio was determined by the O(511 eV)/Pu(317 eV) first derivative peak-to-peak heights for AES and the O(1s)/Pu($4f_{7/2}$) peak areas for XPS. The results are tabulated in Table I. The binding energies for Pu($4f_{7/2}$), C(1s), and

Table I

Oxygen, plutonium ratio (AES-peak-to-peak heights, XPS-peak areas) binding energies (Pu[$4f_{7/2}$], C[1s], O[1s]) and Pu($4f_{7/2}$) FWHM for vacuum heat treatements.

TIME	TEMP	AES	XPS	BINDING ENERGY (eV)			FWHM (eV)
(°C)	(MIN)	O(511eV)/Pu(317eV)	O(1s)/Pu($4f_{7/2}$)	Pu($4f_{7/2}$)	C1S	O1S	Pu($4f_{7/2}$)
22	--	9.8	0.318	426.2, 424.3[a]	284.6	530.1	3.2
150	30	6.7	0.176	424.4	284.8	530.0	2.8
250	30	5.8	0.132	424.2	284.2	529.7	3.3
300	30	5.5	0.154	424.3	284.2	529.9	3.3
400	30	4.9	0.143	424.3	283.6 281.1	529.8	3.6
500	30	3.7	0.129	424.0	280.9	529.7	4.0
500	30	2.6	0.081	423.7	281.2	530.1	4.1
500	30	3.8	0.138	424.0	281.2	530.0	4.0
500	120	3.4	0.093	423.6	281.0	530.0	3.8

[a] shoulder

O(ls) and the Pu($4f_{7/2}$) FWHM are also presented. Notice that the O/Pu ratios become smaller as the temperature increases indicating that the oxide is being reduced by a reaction of the substrate metal with the oxide. This is consistent with the binding energy shifts occurring in the Pu($4f_{7/2}$) peak.

CONCLUSIONS

The surface spectroscopic data (XPS, AES) shows that beginning at about 400°C a new carbon state starts to form. Also the XPS Pu $4f_{7/2}$ binding energy shift and increase in FWHM indicates that the oxide state has changed. This evidence suggests that in reaction (2), the compound formed is not PuO but plutonium oxycarbide [Pu(C,O)].

With the data obtained in this study and a previous report,[5] assignments to the Pu($4f_{7/2}$) binding energy for PuO_2, $PuO_{1.52}$ (α-Pu_2O_3), Pu(C,O), and Pu metal are 426.1, 424.4, 423.6, and 422.2, respectively.

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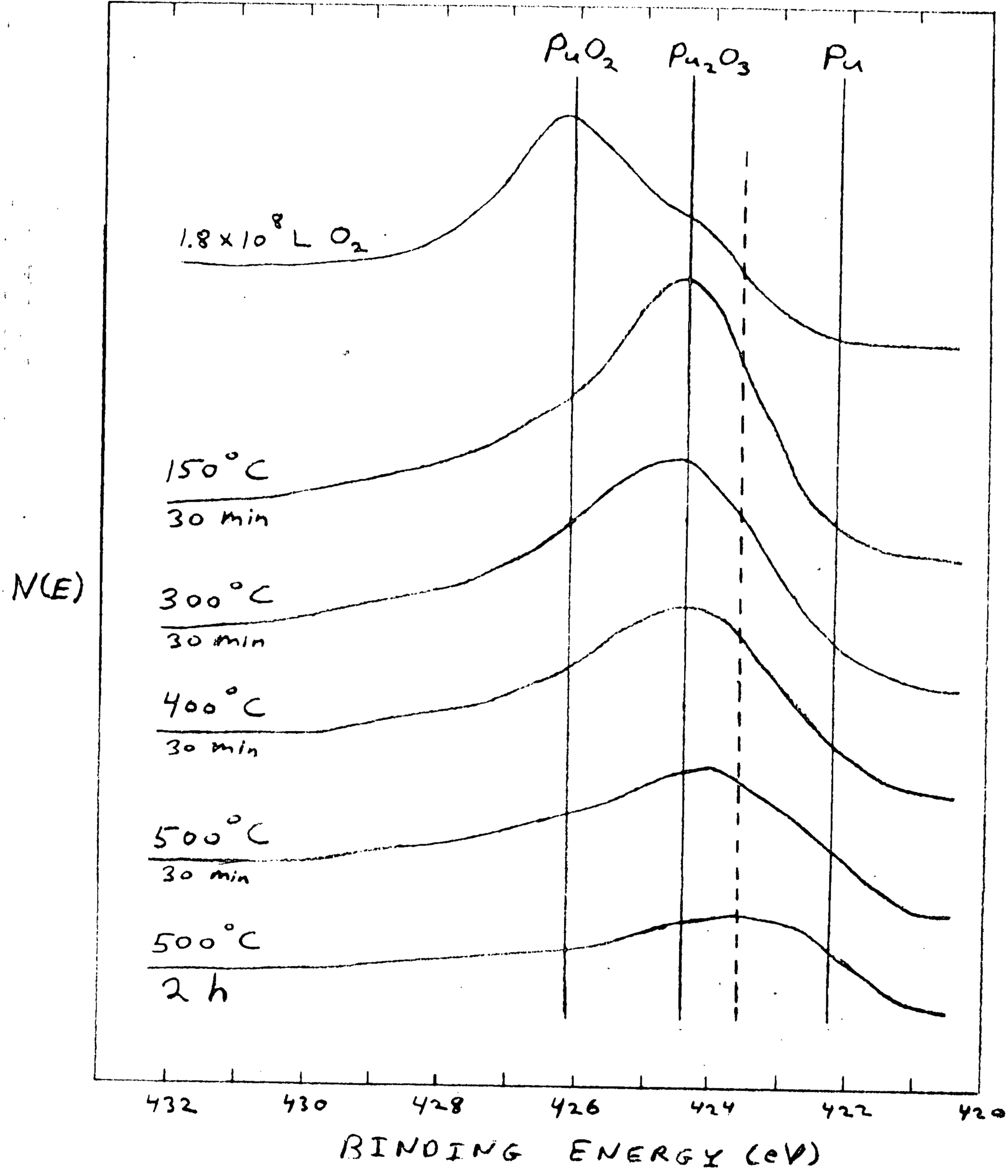


Figure 1. Changes in Pu (4f$_{7/2}$) peak after vacuum heat treatments.

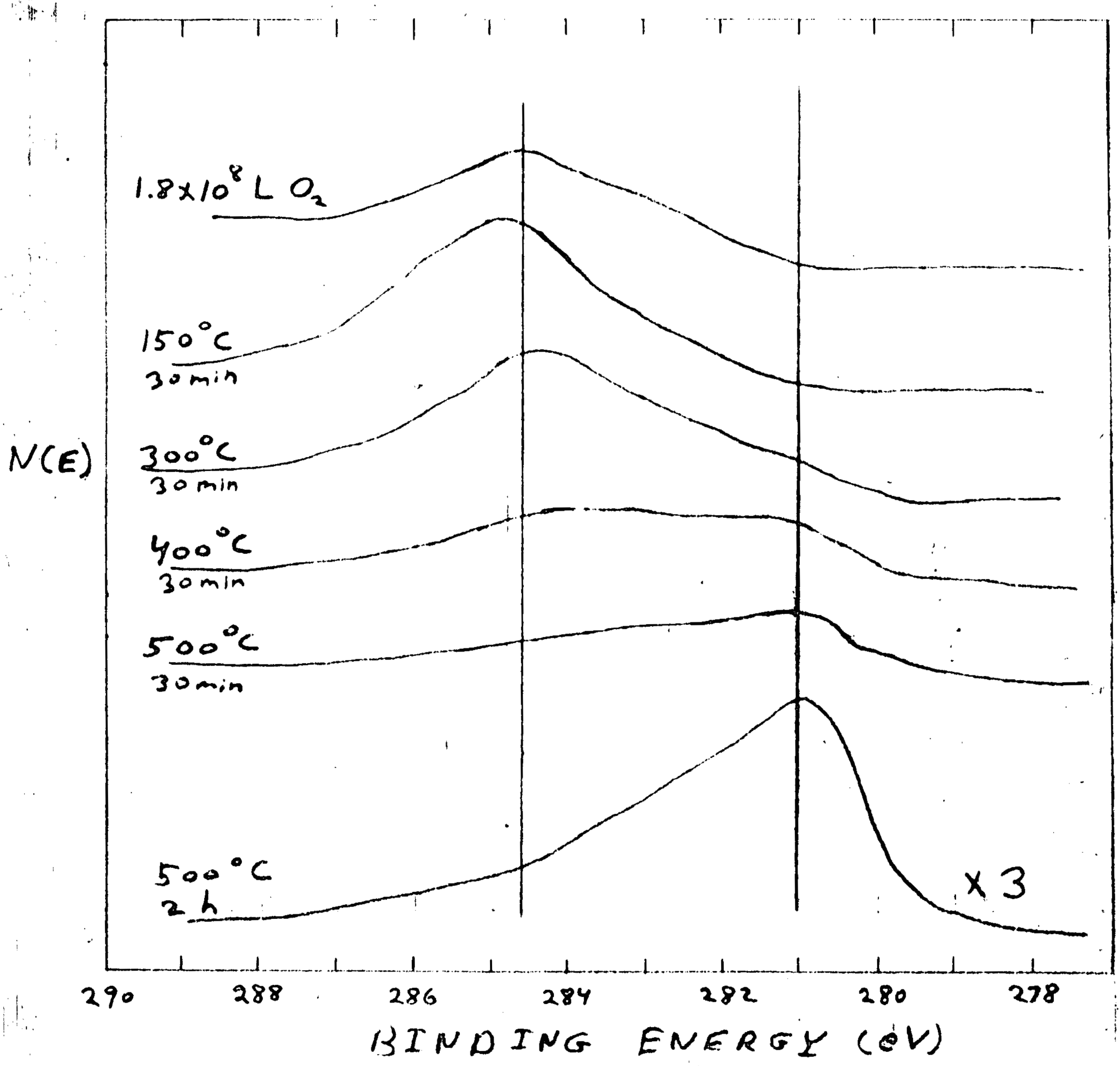
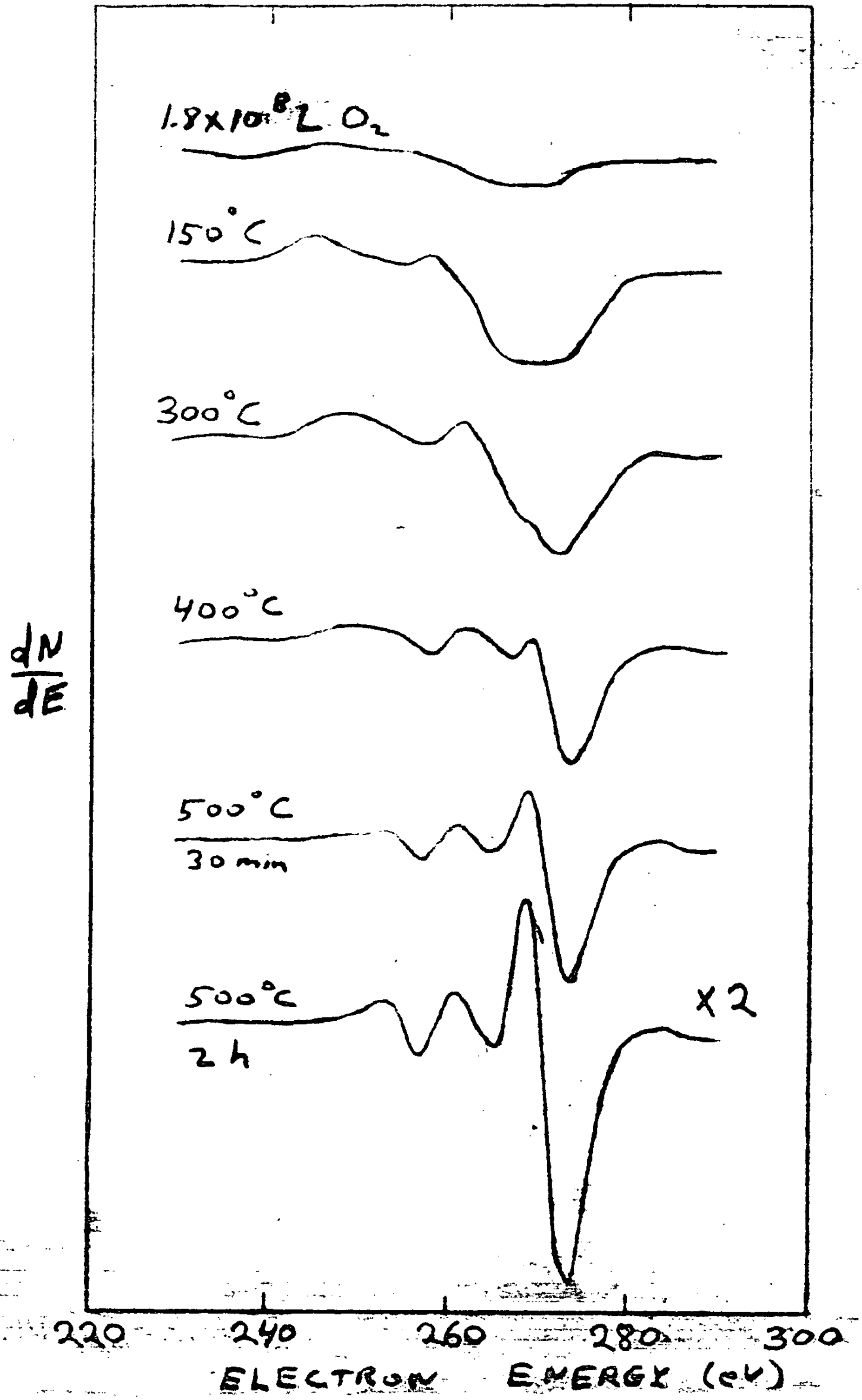


Figure.2. Changes in C(1s) peak after vacuum heat treatments.


1.8x10^8 L O₂
150°C
300°C
400°C
500°C
30 min
500°C
2 h
X2
dN/dE
220
240
260
280
300
ELECTRON ENERGY (eV)