



Auger electron spectroscopic study of the oxidation of oxygen-saturated polycrystalline zirconium  
by Ramazan Kahraman

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
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Abstract:

Zirconium dioxide ( $ZrO_2$ ) is an active catalyst for isosynthesis (hydrogenation) reactions in the conversion of carbonaceous fuels to gaseous and liquid fuels. An enhanced understanding of the catalytic mechanism of surface reactions on  $ZrO_2$  will provide fundamental information toward the development of improved technical hydrogenation catalysts for fuel conversion processes.

A model  $ZrO_2$  test catalyst was developed and characterized for utilization in subsequent investigations of the catalytic properties of  $ZrO_2$  using high vacuum electron and ion spectroscopic methods. The catalytic surface was constituted of a thin  $ZrO_2$  surface layer on an oxygen-saturated polycrystalline zirconium metal substrate. This electrically conductive substrate provides for the dissipation of surface electrical charge during spectroscopic studies of the  $ZrO_2$  surface.

The surfaces developed in this study were analyzed by Auger Electron Spectroscopy (AES). AES, together with ion etching equipment (sputtering), was utilized to measure the stoichiometry, thickness and compositional depth profiles of the  $ZrO_2$  surface layers formed on oxygen-saturated zirconium substrates at several temperatures and extents of  $O_2$  exposure.

It was found that the thickness of the  $ZrO_2$  surface layer formed increased with  $O_2$  exposure temperature up to about 900 K and then decreased at higher exposure temperatures. The oxide layer formed at 900 K has a partially reduced surface if it is cooled in vacuum after oxidation. Cooling the oxidized sample in  $O_2$  eliminates this reduction, retaining the full oxidation of the surface. The  $ZrO_2$  surfaces formed are stable up to about 900 K. The outermost surface becomes reduced at or above 900 K, but the oxide layer under that thin reduced surface remains stable at temperatures up to as high as 1200 K.

AUGER ELECTRON SPECTROSCOPIC STUDY OF THE OXIDATION OF  
OXYGEN-SATURATED POLYCRYSTALLINE ZIRCONIUM

by

Ramazan Kahraman

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APPROVAL

of a thesis submitted by

Ramazan Kahraman

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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## ABSTRACT

Zirconium dioxide ( $ZrO_2$ ) is an active catalyst for isosynthesis (hydrogenation) reactions in the conversion of carbonaceous fuels to gaseous and liquid fuels. An enhanced understanding of the catalytic mechanism of surface reactions on  $ZrO_2$  will provide fundamental information toward the development of improved technical hydrogenation catalysts for fuel conversion processes.

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The surfaces developed in this study were analyzed by Auger Electron Spectroscopy (AES). AES, together with ion etching equipment (sputtering), was utilized to measure the stoichiometry, thickness and compositional depth profiles of the  $ZrO_2$  surface layers formed on oxygen-saturated zirconium substrates at several temperatures and extents of  $O_2$  exposure.

It was found that the thickness of the  $ZrO_2$  surface layer formed increased with  $O_2$  exposure temperature up to about 900 K and then decreased at higher exposure temperatures. The oxide layer formed at 900 K has a partially reduced surface if it is cooled in vacuum after oxidation. Cooling the oxidized sample in  $O_2$  eliminates this reduction, retaining the full oxidation of the surface. The  $ZrO_2$  surfaces formed are stable up to about 900 K. The outermost surface becomes reduced at or above 900 K, but the oxide layer under that thin reduced surface remains stable at temperatures up to as high as 1200 K.

## INTRODUCTION

Zirconia ( $ZrO_2$ ) is an active catalyst for the reduction of carbon oxides (CO and  $CO_2$ ) by hydrogen to form C4 to C8 branched chain hydrocarbons [1]. The hydrogenation of carbon oxides are technically important reactions in the conversion of carbonaceous fuels to gaseous and liquid fuels. Improved technical hydrogenation catalysts may be developed for fuel conversion processes by an enhanced understanding of the catalytic mechanism of surface reactions on  $ZrO_2$ .

The principal fundamental investigations of the catalytic mechanism of these reactions have used bulk  $ZrO_2$  test catalysts [2,3,4]. These catalytic investigations have utilized surface measurement techniques which can be directly applied to electrically insulating refractory substrates, principally Temperature Programmed Desorption (TPD) [2,4] and Fourier Transform Infrared Spectroscopy (FTIR) [3,4]. The understanding of the catalytic activity of  $ZrO_2$  will be significantly enhanced through studies utilizing the additional advanced surface analytical techniques like X-Ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), Auger Electron Spectroscopy (AES), Static Secondary Ion Mass Spectroscopy

(SSIMS), and High Resolution Electron Energy Loss Spectroscopy (HREELS). These surface analytical techniques involve either electron or ion bombardment and/or electron or ion emission from the test surface, requiring some mode of surface charge dissipation during testing.

The specific objective of this research is to develop and characterize a model  $ZrO_2$  test catalyst surface on a conductive substrate which has the potential to be directly utilized in these advanced surface analytical systems.

## BACKGROUND

There have been no published studies of the catalytic properties of the surface oxide layer on bulk Zirconium (Zr) metal. This cohesive surface oxide forms when the highly electropositive Zr is exposed to oxygen. It has been shown that the surface oxide layer has a  $ZrO_2$  stoichiometry [5]. Zr metal is therefore a primary candidate for conductive (charge dissipating) substrate for the model  $ZrO_2$  test catalysts.

Oxygen has been shown to chemisorb on Zr over the first 2 [6] or 3.5 [5] L (1 L =  $10^{-6}$  Torr.s) of  $O_2$  exposure at room temperature. Additional  $O_2$  exposure results in the formation of nuclei of surface oxide which grow to coalescence. The oxide layer is complete at an  $O_2$  exposure of 30 to 60 L and has a thickness of approximately 2 nm [5,6]. Because the diffusion of  $O_2$  through  $ZrO_2$  is very slow, the formation of a thin  $ZrO_2$  surface layer on Zr protects the underlying metal from further significant oxidation at 300 K. However, at higher temperatures, increased oxygen diffusivity in Zr results in oxygen permeation into the bulk metal from the surface oxide layer at measurable rates [7]. As seen in the Zr-oxygen phase

diagram, Figure 1, the oxide film will not be stable if the atomic fraction of oxygen in the bulk Zr is lower than about 0.29 [8]. The bulk Zr, which has a hcp crystal structure commonly designated  $\alpha$ -Zirconium at temperatures below 1135 K, absorbs this oxygen without appreciable change in the hcp lattice constants until the atomic fraction of oxygen is about 0.29 (oxygen saturated zirconium, designated Zr:Oss) [8].

The utilization of the  $ZrO_2$  surface on a pure Zr substrate, as a model catalyst surface in surface analytical studies, would not be satisfactory because of the loss of the surface oxide layer by dissolution into the bulk metal in high temperature tests. It has been indicated that a  $ZrO_2$  surface layer on a Zr:Oss substrate avoids this high temperature dissolution [9]. Zr:Oss substrates have been prepared in a separate research program [10]. In this research program, model  $ZrO_2$  test surfaces are formed by sputter cleaning Zr:Oss substrates and reoxidizing these surfaces at several temperatures and extents of oxygen exposure. The thickness, composition and stability of these surface oxide layers on Zr:Oss substrates are investigated.

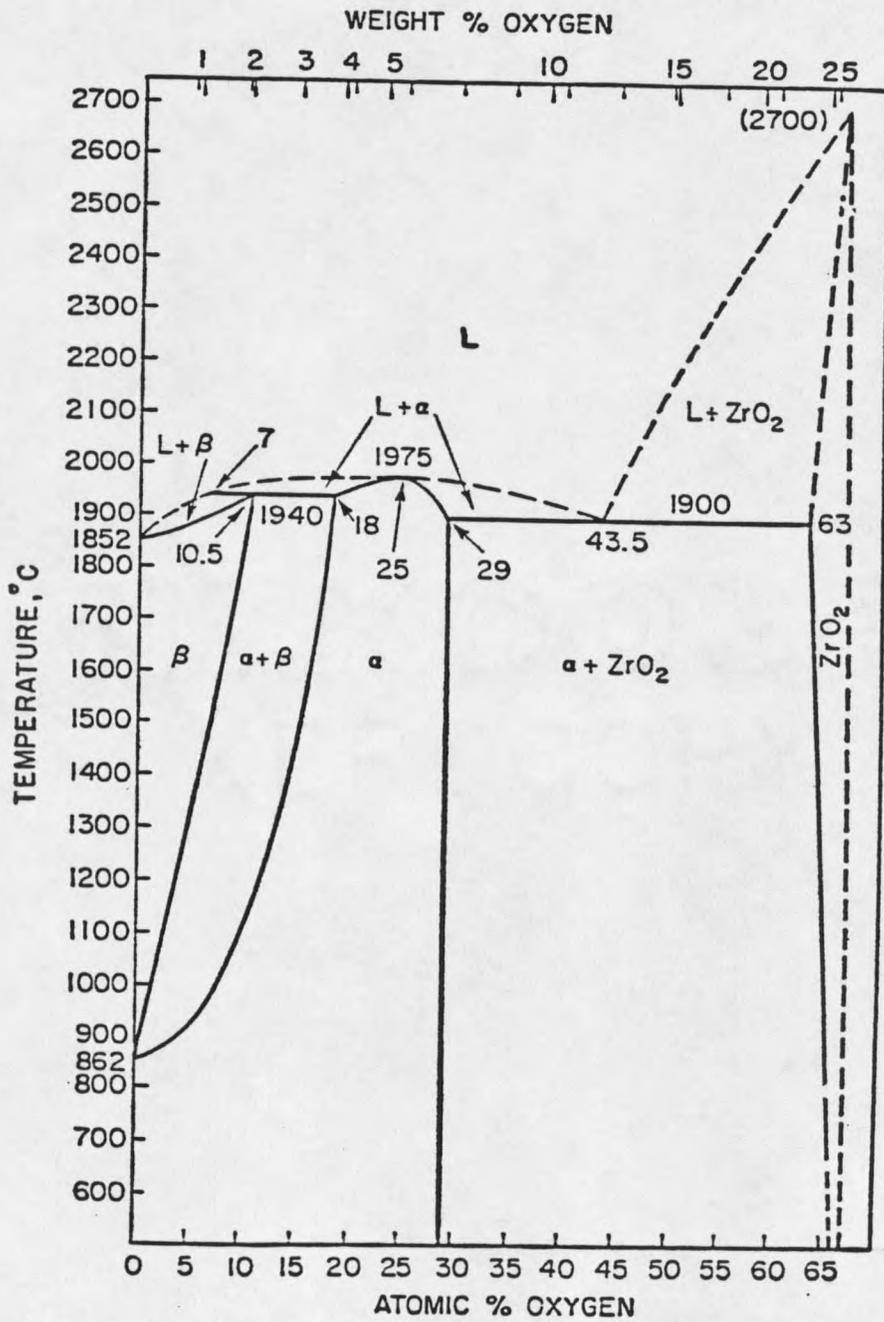


Figure 1. Partial phase diagram of the oxygen-zirconium system

## EXPERIMENTAL METHOD

The primary method of analyzing the surfaces developed in this study was Auger Electron Spectroscopy. AES is based on the Auger process, which is illustrated in Figure 2 [11]. The principle of the technique is that the sample is bombarded by a primary electron beam of between 1 and 10 keV energy which ejects core electrons from an energy level  $E_x$  in the atoms in the surface region of the sample, up to 1  $\mu\text{m}$  or so thick. After this excitation process, the core hole is then filled by an internal process in the ionized atom, whereby an electron from a higher energy level  $E_y$ , either a shallower core level or a valence state, falls into the core hole. The energy lost by this electron ( $E_y - E_x$ ) is taken up by a third electron from an energy level  $E_z$ , also either a shallower core electron or a valence electron. This last electron, called an Auger electron, is then ejected from the atom with an energy  $E_a$ , given approximately by [12]:

$$E_a = E_z + E_y - E_x$$

These Auger electrons are detected by an analyzer that measures their energy and abundance (frequency) of emission.

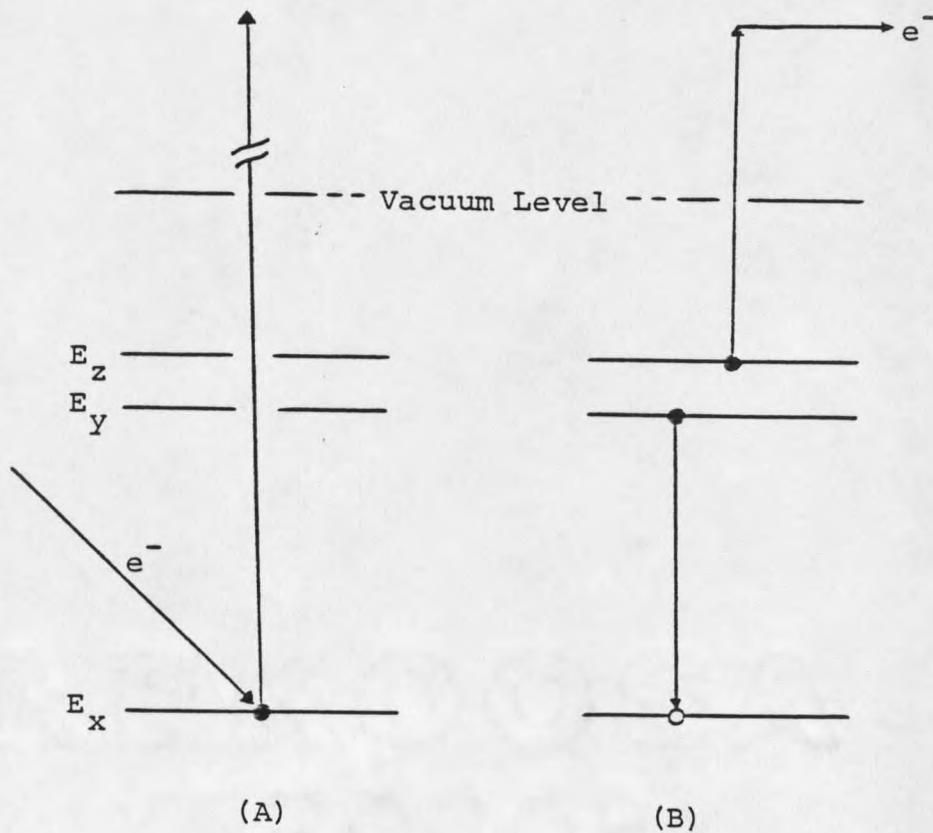


Figure 2. Energy diagram of the Auger process. In a preliminary step (A) a hole is created in the system through excitation by a primary electron which transfers all its energy to a core electron of energy  $E_x$ . The core hole is then filled by the Auger process (B) which involves two other electronic states of the system,  $E_y$  and  $E_z$ .

The whole process, excitation plus Auger recombination, is usually designated using the conventional spectroscopic notations for the initial states of the three electrons involved. For example, if the excitation involves a hole in  $1s$  state and this hole is filled by an electron in the  $2s$  state that transfers its excess energy to another electron in the  $2p$  state, then the entire process is labeled KLL. In this notation the valence states are denoted by the letter V. Because the final energy of the Auger electron is linked to the energies of the three initial states, the emission of Auger electrons at specific energies reveals the presence of certain energy levels in the atoms near the surface under study. Since there are patterns of electron energy levels characteristic of each element, the energy distribution of Auger electrons reveal the presence of specific elements near the surface [11]. The Auger electrons thus have unique energies for each atom and, if the energy spectrum from about 0 to 2 keV is analyzed, the energies of the Auger electron peaks allow for the identification of the surface elements present, except hydrogen and helium. The reason that AES is a surface-sensitive technique lies in the intense inelastic scattering that occurs for electrons in this energy range. Only Auger electrons from the top few atomic layers of a solid survive to be ejected and measured [12].

Figure 3 shows an example of Auger spectrum from a clean Zr surface. The most prominent Auger peaks at about 89, 114, 122, 144 and 172 eV are characteristic of Zr. The weak Auger peaks at about 215, 270 and 506 eV are Auger transitions from contaminants of Ar, C and oxygen, respectively. The increase in background intensity with electron energy consists mainly of backscattered primary electrons and inelastically scattered Auger electrons [13].

Quantitative analysis is also possible utilizing AES, as discussed in the Experimental Procedure section. One of the most interesting applications of quantitative Auger analysis is the depth profiling technique, in which surface atoms are removed by sequential ion bombardment with intermediate analysis of surface composition by AES. The equipment used in AES depth profiling is equivalent to a standard Auger spectrometer except for the presence of an ion gun. The ion gun is used to bombard the surface of the sample with ions of an inert gas, usually argon. The bombardment can be used to remove the surface atoms of the sample at a relatively slow rate, almost atomic layer by atomic layer. If a quantitative Auger analysis is carried out during interruptions in the ion bombardment, the results yield the composition of the sample at different depths with respect to the original surface [11].

In this study, AES, together with ion etching equipment

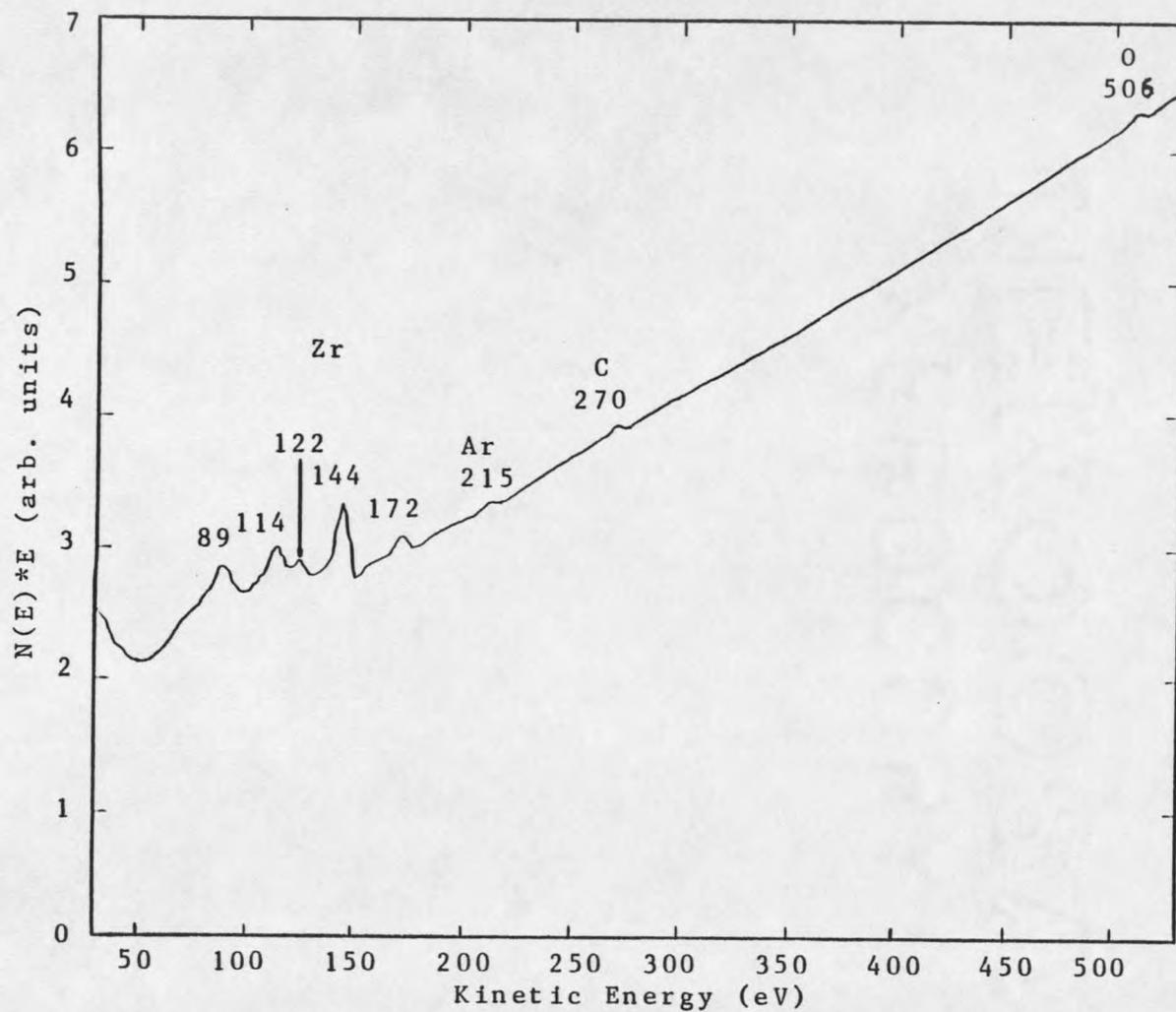


Figure 3. The AES spectrum from 30 eV to 530 eV for a sputter-cleaned Zr sample

(sputtering), is utilized to measure the stoichiometry, thickness and compositional depth profiles of the  $ZrO_2$  surfaces formed on sputter-cleaned  $Zr:O_{ss}$  substrates at several temperatures and extents of  $O_2$  exposure.

## EXPERIMENTAL SYSTEM

The experimental system used in this study was the PHI 595 scanning Auger microprobe located in the Center for Research in Surface Science and Submicron Analysis (CRISS) at Montana State University. This system has a base pressure of  $2 \times 10^{-10}$  Torr and can be pumped by a  $110 \text{ ls}^{-1}$  turbopump, a  $200 \text{ ls}^{-1}$  ion pump and a titanium sublimation pump. The electron gun incorporated in this system is capable of producing a primary electron beam energy in the range of 0 to 30 keV. In this study, the primary electron beam had a voltage of 3 keV and a beam current of approximately  $0.20 \text{ }\mu\text{A}$ , which corresponds to an electron beam diameter of about  $0.80 \text{ }\mu\text{m}$ . The electron energy analyzer is a cylindrical mirror analyzer. The system also includes a differentially pumped argon ion gun. It is used for surface cleaning and depth profiling. The energy of argon ions used for surface sputtering was 3.0 keV. The AES and sputter time data were recorded digitally on magnetic discs with the use of an integral DEC PDP 11/04 computer.

## EXPERIMENTAL PROCEDURE

Two zirconium samples were utilized. One was a 99.99 percent pure, 0.025 mm thick polycrystalline foil 4 mm x 10 mm in size. The second was a polished Zr:Oss sample 0.25 mm thick and approximately 4 mm x 8 mm in size, which was formed by saturating a 99.99 percent pure polycrystalline foil with oxygen [10].

The Zr:Oss specimen was mounted on a Ta foil backing. The Ta foil was spot welded to Ta support wires connected to two large copper feedthroughs allowing resistive heating of the sample. The temperature measurement of the specimen was made by a W-5% Re/W-26% Re thermocouple welded to the back of the Ta foil mount. The temperatures employed varied between room temperature and 1200 K. All tests on pure Zr were performed at room temperature.

The AES measurements were made by rastering the electron beam over a 0.06 mm x 0.06 mm area. A phosphor foil was utilized to ensure that this area was central to 2 mm x 2 mm area cleaned by a rastered Ar<sup>+</sup> beam during the ion bombardment of the surface. All AES measurements were conducted at room temperature.

Two primary types of AES scans were performed. One

involved additive multiple scans from 30 eV to 530 eV to detect the primary Zr and oxygen Auger peaks, as well as evidence of other elements on the surface, with Auger peak energies in this region. The second type of AES scan focused primarily on Zr and oxygen features by multiplexing selected energy regions. One multiplexed region was between 78 eV and 178 eV to detect the primary Zr Auger peaks and the other between 495 eV and 515 eV for oxygen detection.

Utilizing a conventional method for quantitative analysis [14], the surface oxygen atomic fraction ( $X_O$ ) can be determined by:

$$X_O = \frac{P_O/S_O}{P_O/S_O + P_{Zr}/S_{Zr}} \quad (1)$$

where  $P_O$  and  $P_{Zr}$  are the peak-to-peak heights in the differentiated spectrum, and  $S_O$  and  $S_{Zr}$  are the relative sensitivity factors of the oxygen and Zr peaks, respectively. The AES spectra taken during depth profiles of the oxidized substrates were automatically differentiated by the PHI software designed for depth profiling. The resulting peak-to-peak heights were used to develop compositional profiles. The intensity of the Auger peak at 89 eV is generally superior as a monitor of the surface abundance of Zr since the intensity of the more commonly utilized 144 eV

peak is strongly dependent on the oxidation state of Zr [7,15,16,17]. The relative sensitivity factor ( $S_{Zr}^{144}$ ) of 144 eV peak is 0.22 [15]. Similar compositions were obtained on sputter cleaned Zr substrates if the relative sensitivity factor ( $S_{Zr}^{89}$ ) of the 89 eV peak was set at 0.096. Thus, surface oxygen concentrations were determined employing the 89 eV peak for Zr and the 506 eV peak for oxygen, and 0.5 and 0.096 for  $S_O$  [14] and  $S_{Zr}^{89}$ , respectively. Note: The peak energies in the differentiated ( $d[N(E)*E]/dE$  vs.  $E$ ) spectra are somewhat higher, by about 2 eV, than peak positions (in  $N(E)*E$  vs.  $E$  spectra) presented in this thesis for clean Zr. Effects of impurity carbon and implanted Ar were neglected, since they were assumed to have little influence on the atomic ratio of oxygen to zirconium.

During depth profiling, Auger intensities were established by scanning the region between 80 and 95 eV for 15 seconds to measure the Zr 89 eV peak and the region from 495 eV to 515 eV for 20 seconds for the oxygen 506 eV peak. These intensity measurements were performed automatically during programmed interruptions in the argon ion sputtering of the surface. The duration of the individual sputters was chosen to be 30 seconds, since the time for the  $Ar^+$  beam to achieve stability would significantly affect the results for shorter sputter times. Figure 4 shows an example of a depth profile (peak-to-peak height vs. sputter time), which was

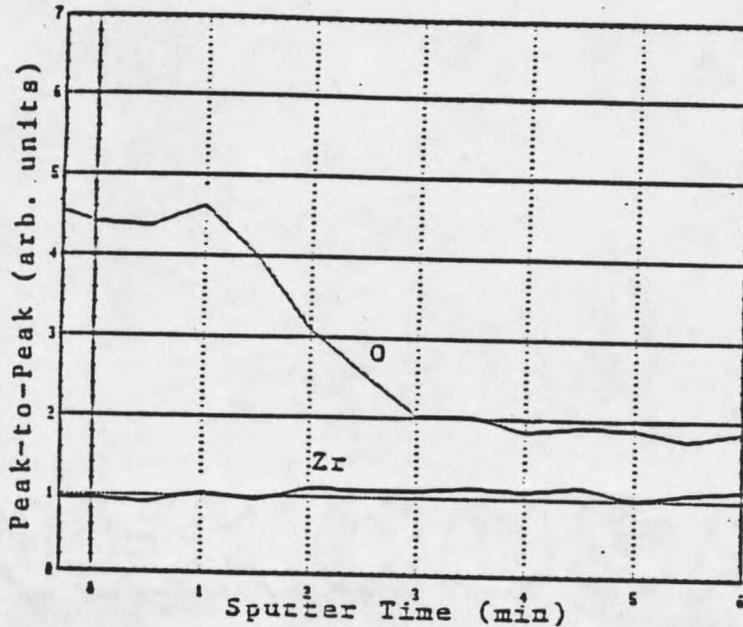


Figure 4. The AES depth profile, as peak-to-peak height vs. sputter time, conducted on Zr:Oss after 300 L O<sub>2</sub> exposure at 700 K

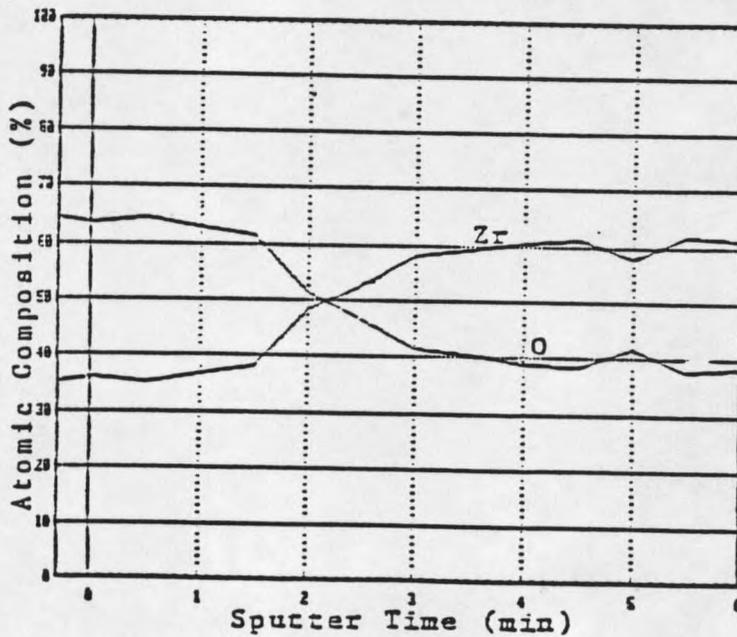


Figure 5. The AES depth profile, as atomic composition vs. sputter time, conducted on Zr:Oss after 300 L O<sub>2</sub> exposure at 700 K

conducted on Zr:Oss after 300 L O<sub>2</sub> exposure at 700 K. The compositional depth profile (atomic composition vs. sputter time) shown in Figure 5 was obtained by a subroutine of the PHI software utilizing Equation 1 on the depth profile intensities plotted in Figure 4. The two peak-to-peak and composition values recorded before sputtering is initiated are for the original surface. The surface oxygen concentration was calculated to be about 64 atomic percent before the sputtering and about 38 atomic percent at the end of twelve 30-second sputter cycles.

The experimental system had a sputter rate of 81 Å/min for SiO<sub>2</sub>, which has been established using an oxide standard (460 Å SiO<sub>2</sub> on Si metal). The ratio of the sputter rates of SiO<sub>2</sub> and ZrO<sub>2</sub> has been measured to be 0.14/0.12 using 4 keV argon ions [18]. In this study, sputtering was carried out using 3.0 keV argon ions. This change in ion energy should not significantly change the ratios of sputter rates. Hence, the sputter rate of the ZrO<sub>2</sub> surface layer on the oxidized substrates is assumed to be about 69 Å/min in this study. The thickness of the ZrO<sub>2</sub> layers formed on Zr:Oss substrates were determined by multiplying this sputter rate and the sputter time, indicated in the depth profiles, up to the time at which the surface oxygen concentration starts to decrease from a constant (about 67 atomic percent) value.

For those tests in which the surface was not sputtered,

the surface oxygen concentration was determined by a different method than that utilized in the automated depth profile subroutine. The following equation [19] was used in the manual evaluation of surface oxygen concentration.

$$X_O = \frac{K(A_O/A_{Zr})}{1 + K(A_O/A_{Zr})} \quad (2)$$

where  $X_O$  is the surface oxygen atomic fraction,  $A_O$  and  $A_{Zr}$  are the peak areas (integrated spectral intensities) in the AES spectrum for oxygen and zirconium, respectively and  $K$  is a constant which is determined utilizing a surface whose oxygen concentration is known. The 89 eV and 506 eV Auger peaks were employed for zirconium and oxygen, respectively. The peak areas were measured using the PHI software designed for this procedure. The program provides the area between a straight line connecting the selected end points on the background spectra and the spectral curve. The end points utilized for the 89 eV peak of Zr were 80 eV and the minimum point on the background spectra occurring between 94 and 99 eV. The oxygen AES peak area was measured by integration of the spectra between 500 and 515 eV. The uncertainty in the background subtraction, which is larger for the Zr 89 eV peak, may add some error to the surface composition values determined by this method.

The constant K in Equation 2 was determined to be 0.26, utilizing the Zr 89 eV and the oxygen 506 eV peak areas for each of the two independent spectra taken for Zr:Oss samples which were oxidized with 300 L O<sub>2</sub> exposure at 900 K followed by cooling in O<sub>2</sub>. The AES spectrum from 78 eV to 178 eV for one of these surfaces is shown in Figure 6, curve b. This surface is most probably fully oxidized to ZrO<sub>2</sub> with a surface oxygen concentration of about 67 atomic percent. The second oxidized sample revealed a surface oxygen concentration of about 67 atomic percent during automated depth profiling. Curve a in Figure 6 is for Zr:Oss cooled in vacuum after 300 L O<sub>2</sub> exposure at 900 K, and will be discussed later.

The procedure employed in each test involved cleaning the sample by Ar<sup>+</sup> bombardment until the surface oxygen concentration detected by AES was negligible for pure Zr or constant for a Zr:Oss sample. After the temperature adjustment of the sample, oxygen was admitted into the vacuum chamber through a leak valve for the pressure-time values appropriate for the test. The oxygen exposure pressures and the exposure times varied between  $1.0 \times 10^{-7}$  Torr to  $1.0 \times 10^{-6}$  Torr, and 30 seconds to 600 seconds, respectively. Since nearly identical spectra were observed both for repeated cycles of cleaning and oxidation of specific Zr:Oss substrates, and for separate pure Zr

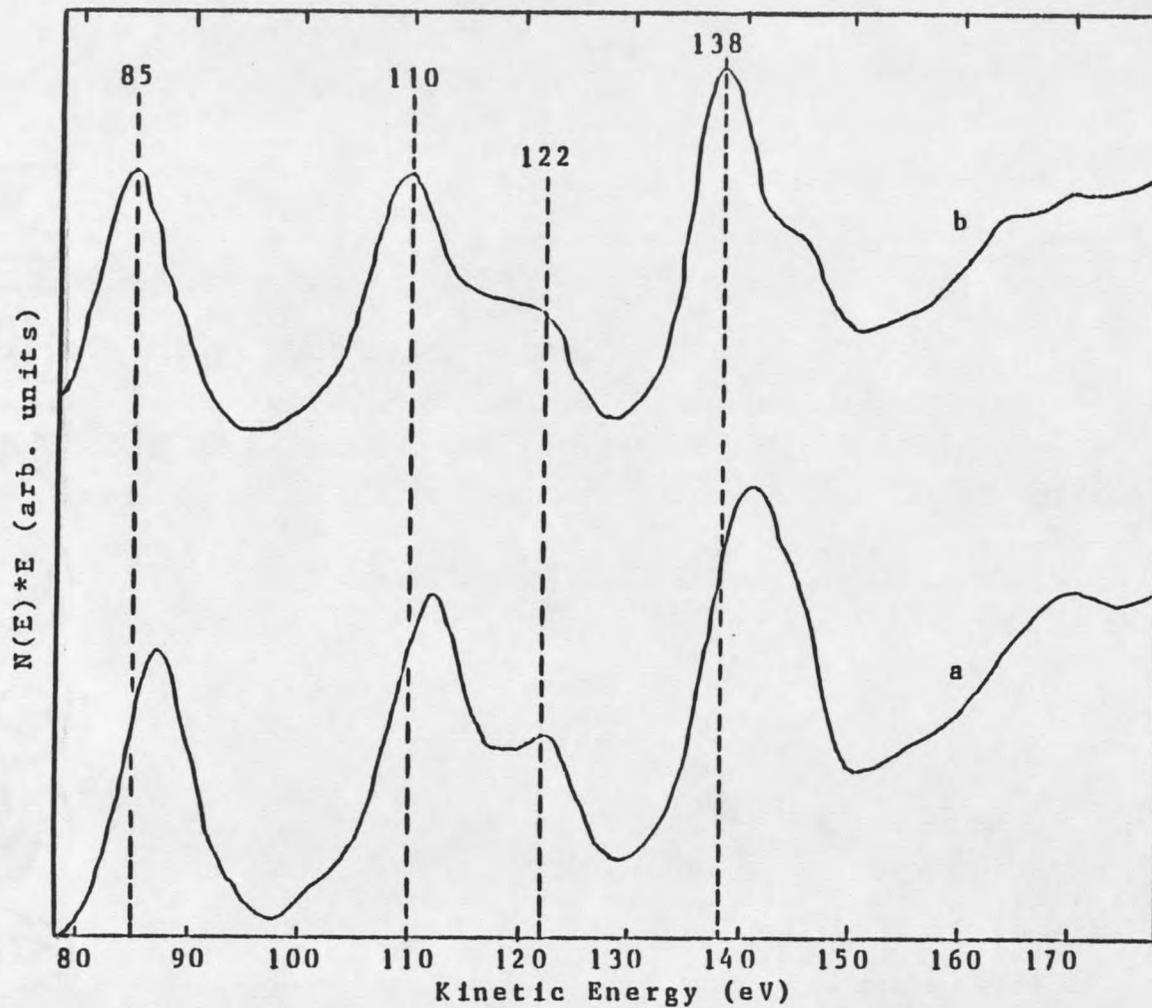


Figure 6. The AES spectrum from 78 eV to 178 eV for: (a) Zr:Oss cooled in vacuum after 300 L O<sub>2</sub> exposure at 900 K; (b) Zr:Oss cooled in 1.0x10<sup>-6</sup> Torr O<sub>2</sub> after 300 L O<sub>2</sub> exposure at 900 K













































































