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

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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Ramazan Kahraman

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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.

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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 α-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.

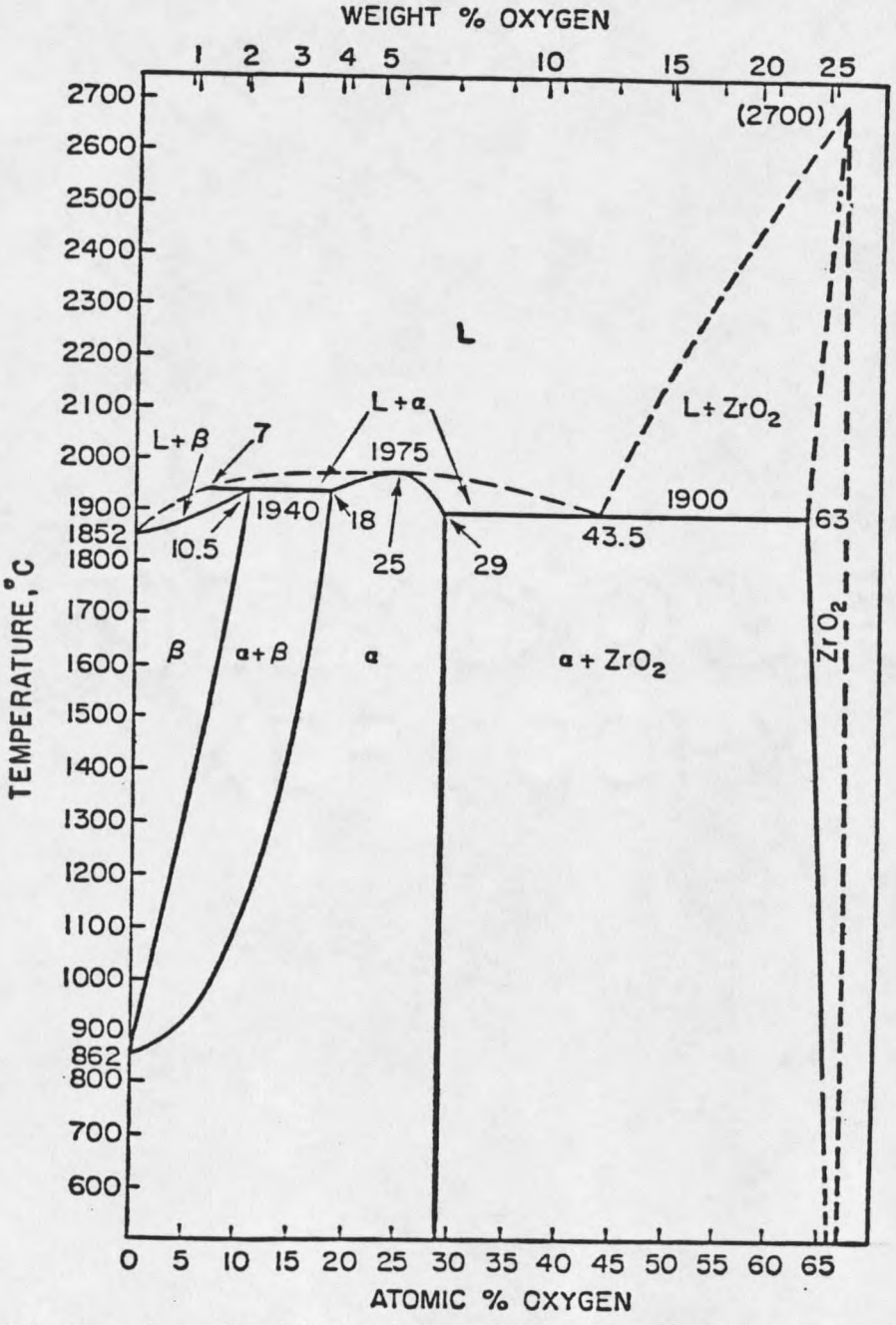

Figure 1. Partial phase diagram of the oxygen-zirconium system

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 μm 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.

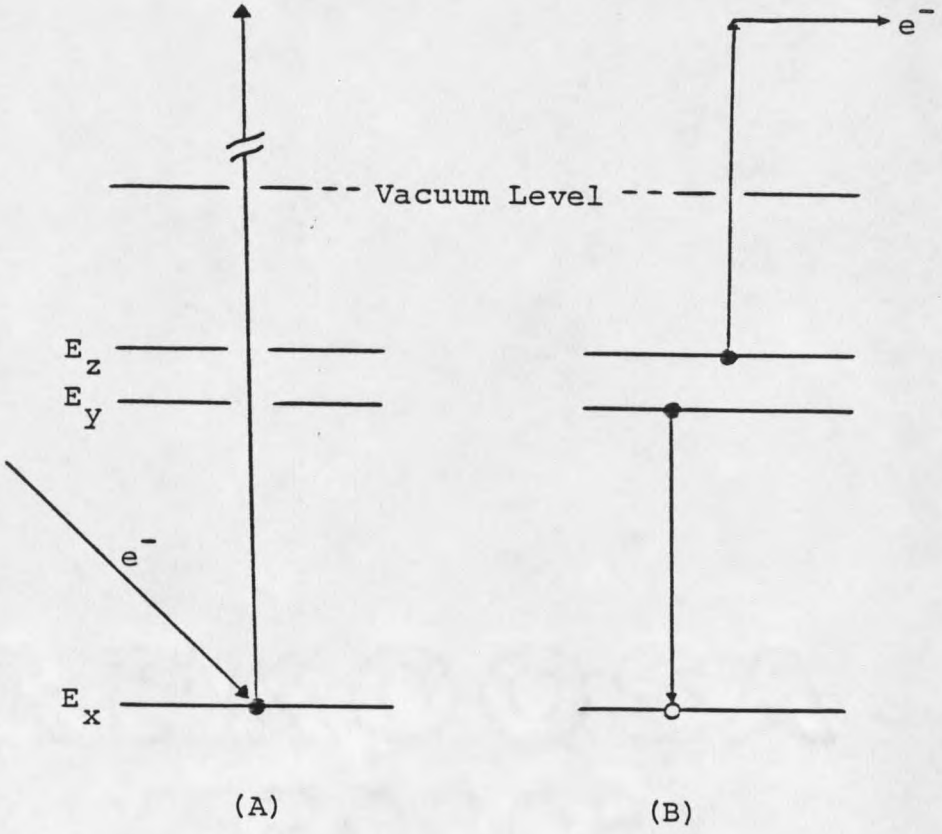

Figure 2. Energy diagram of the Auger process. In a preliminary step (A) a hole is created in the system through excitation by a primary electron which transfers all its energy to a core electron of energy E_x. The core hole is then filled by the Auger process (B) which involves two other electronic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

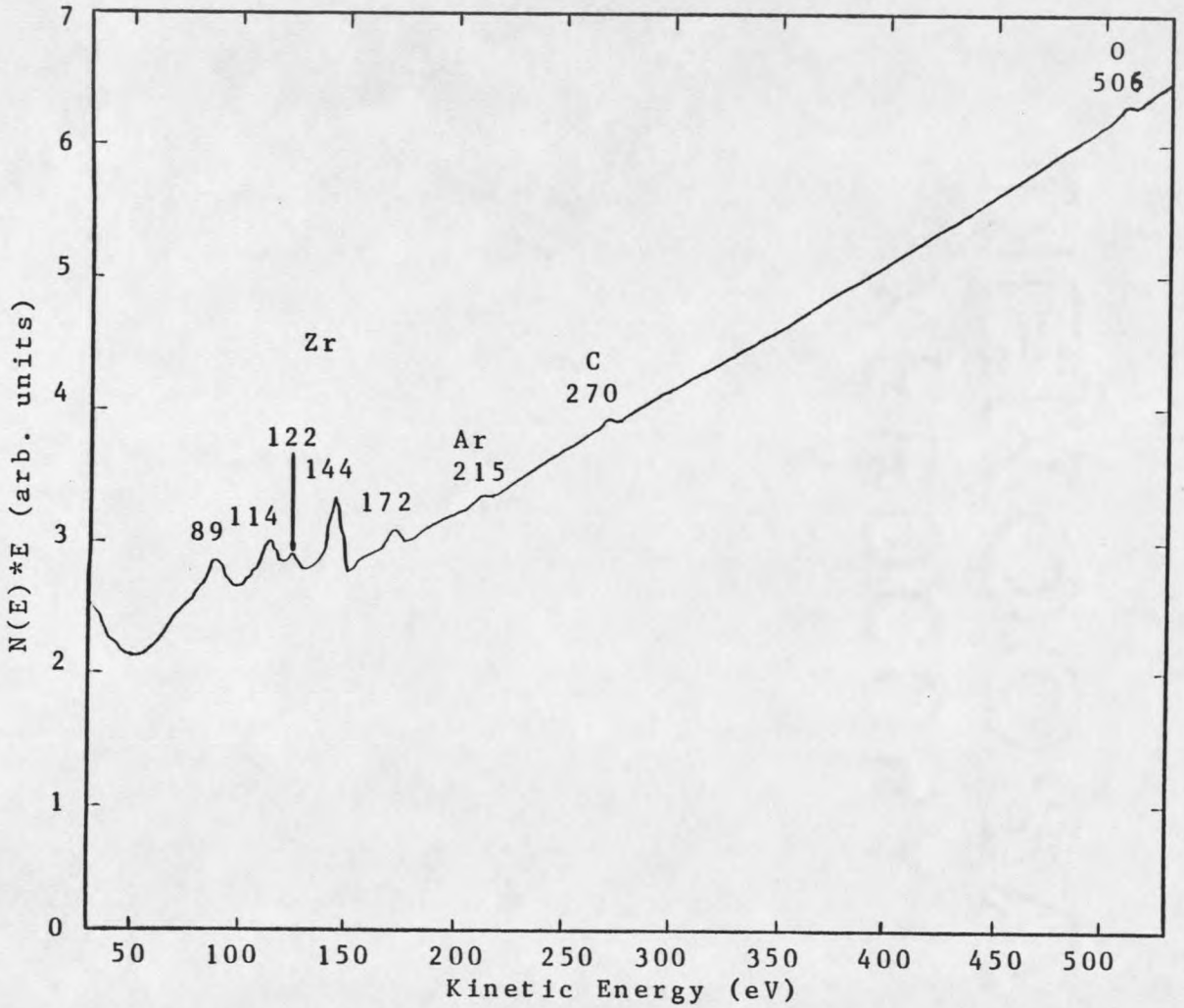

Figure 3. The AES spectrum from 30 eV to 530 eV for a sputter-cleaned Zr sample

(sputtering), is utilized to measure the stoichiometry, thickness and compositional depth profiles of the ZrO_2 surfaces formed on sputter-cleaned Zr:Oss 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 $2x10^{-10}$ Torr and can be pumped by a 110 ls^{-1} turbopump, a 200 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 μA, which corresponds to an electron beam diameter of about 0.80 μm. 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^+ 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:

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

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

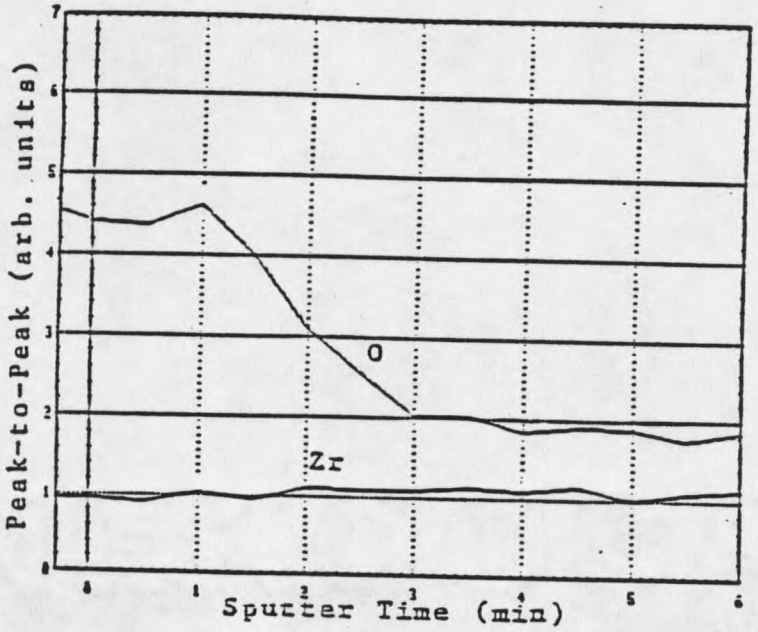

Figure 4. The AES depth profile, as peak-to-peak height vs. sputter time, conducted on Zr:Oss after 300 L O_2 exposure at 700 K

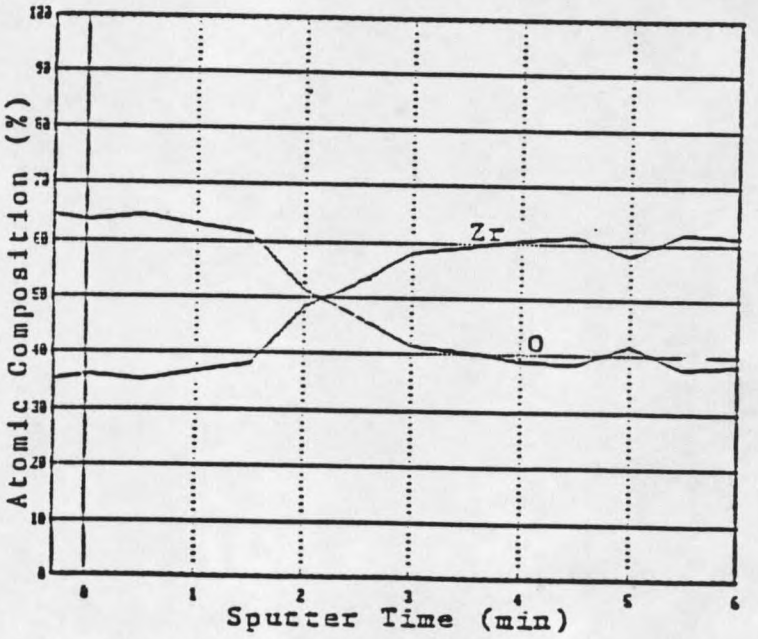

Figure 5. The AES depth profile, as atomic composition vs. sputter time, conducted on Zr:Oss after 300 L O_2 exposure at 700 K

conducted on Zr:Oss after 300 L O_2 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_2, which has been established using an oxide standard (460 Å SiO_2 on Si metal). The ratio of the sputter rates of SiO_2 and ZrO_2 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_2 surface layer on the oxidized substrates is assumed to be about 69 Å/min in this study. The thickness of the ZrO_2 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.

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

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_2 exposure at 900 K followed by cooling in O_2. 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_2 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_2 exposure at 900 K, and will be discussed later.

The procedure employed in each test involved cleaning the sample by Ar^+ 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 1.0×10^{-7} Torr to 1.0×10^{-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

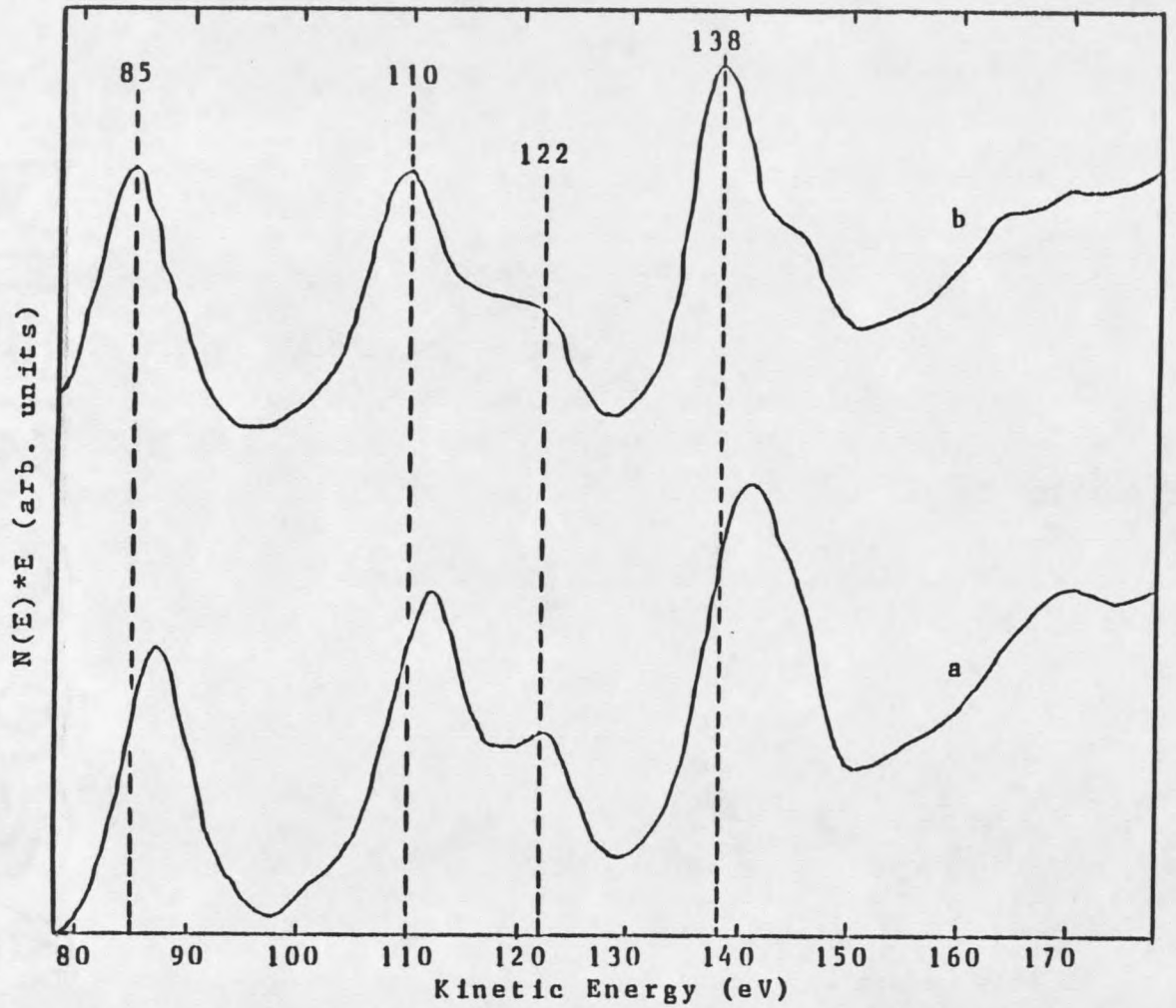

Figure 6. The AES spectrum from 78 eV to 178 eV for: (a) Zr:Oss cooled in vacuum after 300 L O_2 exposure at 900 K; (b) Zr:Oss cooled in 1.0×10^{-6} Torr O_2 after 300 L O_2 exposure at 900 K

substrates, it is improbable that any significant surface contaminants were present.

The spectra are presented in the Results and Discussion section as plots of N(E)*E vs. E. They are used to indicate the state of oxidation of Zr, and determine the surface oxygen concentration utilizing peak areas in addition to the surface oxygen concentration determined during depth profiling.

RESULTS AND DISCUSSION

Auger Spectra of Sputter-Cleaned and Room Temperature Oxidized Pure Zr

The 30 eV to 530 eV AES spectrum of sputter-cleaned Zr foil is presented in Figure 3. The multiplexed spectrum taken on sputter-cleaned Zr in the region of 78 eV to 178 eV, within which the most important Zr Auger peaks occur, is shown in Figure 7. Also shown in Figure 7 are spectra taken on sputter-cleaned Zr:Oss and both substrates after 300 L O_2 exposure at room temperature. The most prominent Zr Auger peaks for the sputter-cleaned Zr surface are the following: MNN peaks at 89 and 114 eV, MNV peaks at 122 and 144 eV and an MVV peak at 172 eV. The three major changes in the AES peaks, after 300 L O_2 exposure on pure Zr, are the new MNV peak at 138 eV (shifted -6 eV relative to clean Zr), the MNN peak at 110 eV (shifted -4 eV) and the MNN peak at 85 eV (shifted -4 eV). Figure 8 shows the AES spectra from 495 eV to 515 eV for sputter-cleaned Zr and for this surface after 300 L O_2 exposure. The main new feature in the spectrum from oxidized Zr, as compared with that observed in the clean Zr spectrum, is the high intensity oxygen KLL peak at 506 eV.

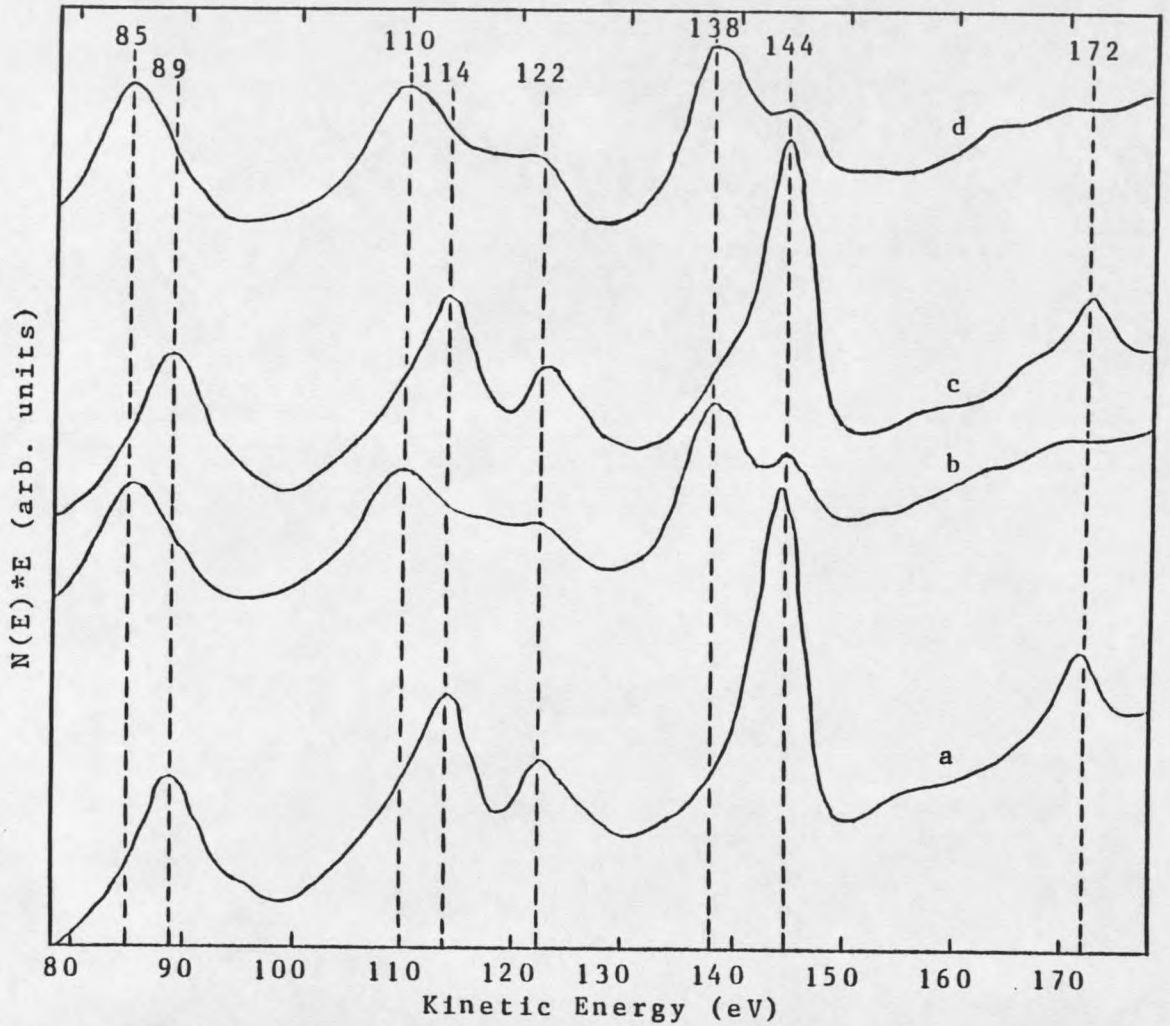

Figure 7. The AES spectrum from 78 eV to 178 eV for: (a) sputter-cleaned Zr; (b) 300 L O_2 exposed Zr at room temperature; (c) sputter-cleaned Zr:Oss; (d) 300 L O_2 exposed Zr:Oss at room temperature

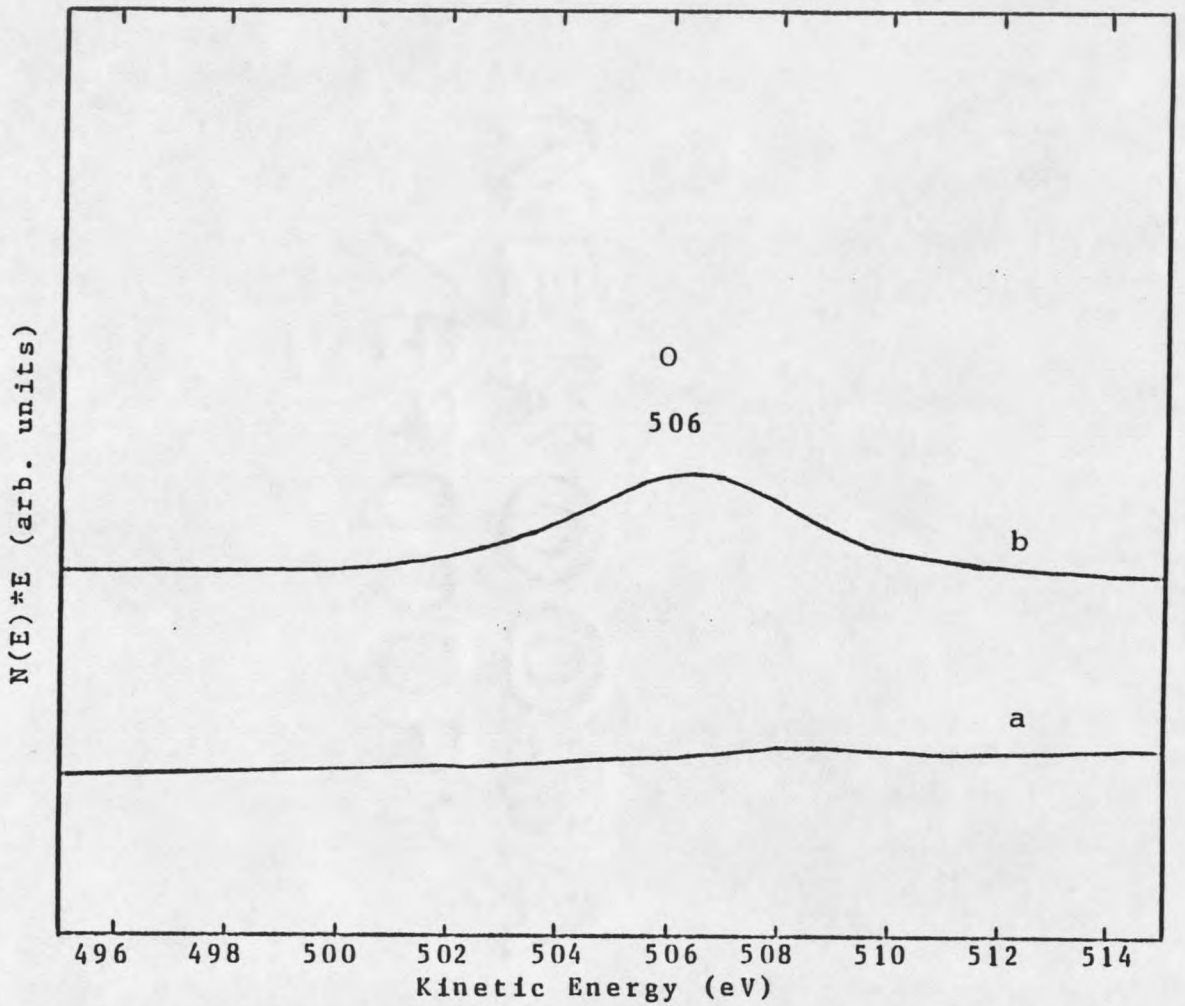

Figure 8. The AES spectrum from 495 eV to 515 eV for: (a) sputter-cleaned Zr; (b) 300 L O_2 exposed Zr at room temperature

The energy shifts of the main Zr-derived AES peaks upon oxidation are indicative of a change in the chemical state of the zirconium atoms in the surface region of the oxidized Zr. The Auger peaks at 89 and 114 eV, arising from core level transitions, exhibit a modest shift of about -4 eV during surface oxide formation. The shift from 144 eV to 138 eV of the MNV peak, involving one valence electron, is larger because the Zr(4d,5s) valence band electrons are transferred to the O 2p valence band of ZrO_2 upon oxidation. This difference in the energy shifts of the main Zr AES peaks attests to the fact that the core level electrons are less affected by the chemical environment than the valence electrons. It has been shown that the Zr MVV peak at 172 eV, involving two valence electrons, decreases so rapidly in intensity with oxygen exposure that no shift can be identified [15]. The strong decrease in the intensity of the 172 eV peak upon oxidation is evident in Figure 7.

The surface oxygen concentration of the pure Zr sample after it was exposed to 300 L O_2 was determined to be about 67 atomic percent by the depth profiling technique, which evidences the existence of ZrO_2 on the surface. The surface oxygen concentration of about 65 atomic percent, established by utilizing peak areas, is not far from the value of 67 percent established during depth profiling. The small peak remaining at 144 eV and the shoulder (at about 122 eV) at

the high energy side of the Zr 110 eV peak in Figure 7 for the 300 L O_2 exposed Zr indicate the presence of some reduced Zr on the surface. This could arise either from an incomplete oxidation of the Zr substrate or from a very thin surface oxide layer. The escape depths are approximately 7 Å for the 144 eV electrons and 6.6 Å for the 122 eV electrons [20]. Hence, if the thickness of the surface oxide layer was less than about 7 Å, the remaining 144 eV and 122 eV peaks could arise from the underlying Zr metal.

The 89 eV peak areas were determined both for clean Zr and oxidized Zr. The rather small change in the area of the 89 eV peak upon oxidation, about 66 percent of the clean surface value, confirms that the strength of this Auger transition is not changed much during oxidation, since it involves only Zr core electrons. Actually, if it was assumed that the strength of the transition and the mean free path at 89 eV were both the same for Zr and ZrO_2 [15], one could obtain an asymptotic value of 67 percent due to the difference in Zr atom density in Zr and ZrO_2 [see Appendix]. This is very close to the observed value of 66 percent.

The observations above are qualitatively in good agreement with the previous studies [15,21,22], in that the energy shifts and the intensity changes of the primary Zr Auger peaks are indicative of a change in the chemical state

of the zirconium atoms in the specimen surface region. The Auger peak (at about 138 eV) at the low energy side of the Zr 144 eV peak is an indication of oxidized zirconium. The degree of attenuation of the Zr Auger peak intensities upon oxidation is primarily related to the number of valence electrons involved in the respective Auger transitions, and secondarily to the decrease in the atomic concentration of Zr as the surface oxide is formed.

Auger Spectra of Sputter-Cleaned and Room Temperature Oxidized Zr:Oss

The AES spectrum between 78 eV and 178 eV for sputter-cleaned Zr:Oss is shown in Figure 7. This spectrum is very similar to the spectrum for clean Zr, except for a small shoulder at the low energy side of the Zr 144 eV peak. This shoulder at about 138 eV indicates a slight oxidation of the Zr:Oss substrate. The surface oxygen concentration was determined by using Equation 1 to be 33 atomic percent, which is not far from the value 29 atomic percent for oxygen saturation as shown in the Zr-oxygen phase diagram, Figure 1 [8].

The lack of significant energy shifts of the main Zr-derived AES peaks or of significant change (about 2 percent increase) in the area of the 89 eV peak, as compared to the

spectrum of pure clean Zr, establishes that there is not a significant change in the chemical state of the surface zirconium atoms in Zr:Oss as compared to pure Zr.

The AES spectrum for Zr:Oss after 300 L O_2 exposure at room temperature is shown in Figure 7. The similarity of this spectrum to the spectrum for oxidized Zr and the surface oxygen concentration of about 67 atomic percent, determined by depth profiling of this oxygen exposed Zr:Oss surface, Figure 9, indicate the existence of ZrO_2 on the surface. The difference in area of the Zr 89 eV peaks of the spectra for oxidized Zr and oxidized Zr:Oss in Figure 7 is less than 10 percent. Again the small peak at 144 eV and the shoulder at the high energy side of the Zr 110 eV peak could either indicate an incomplete surface oxidation or an oxide layer thinner than the escape depth of the Zr Auger electrons, about 7 Å. The compositional depth profile of the room temperature oxidized Zr:Oss in Figure 9 shows that the surface oxide is removed during the first 30-second sputter, indicating that the thickness of the surface oxide layer is less than 35 Å.

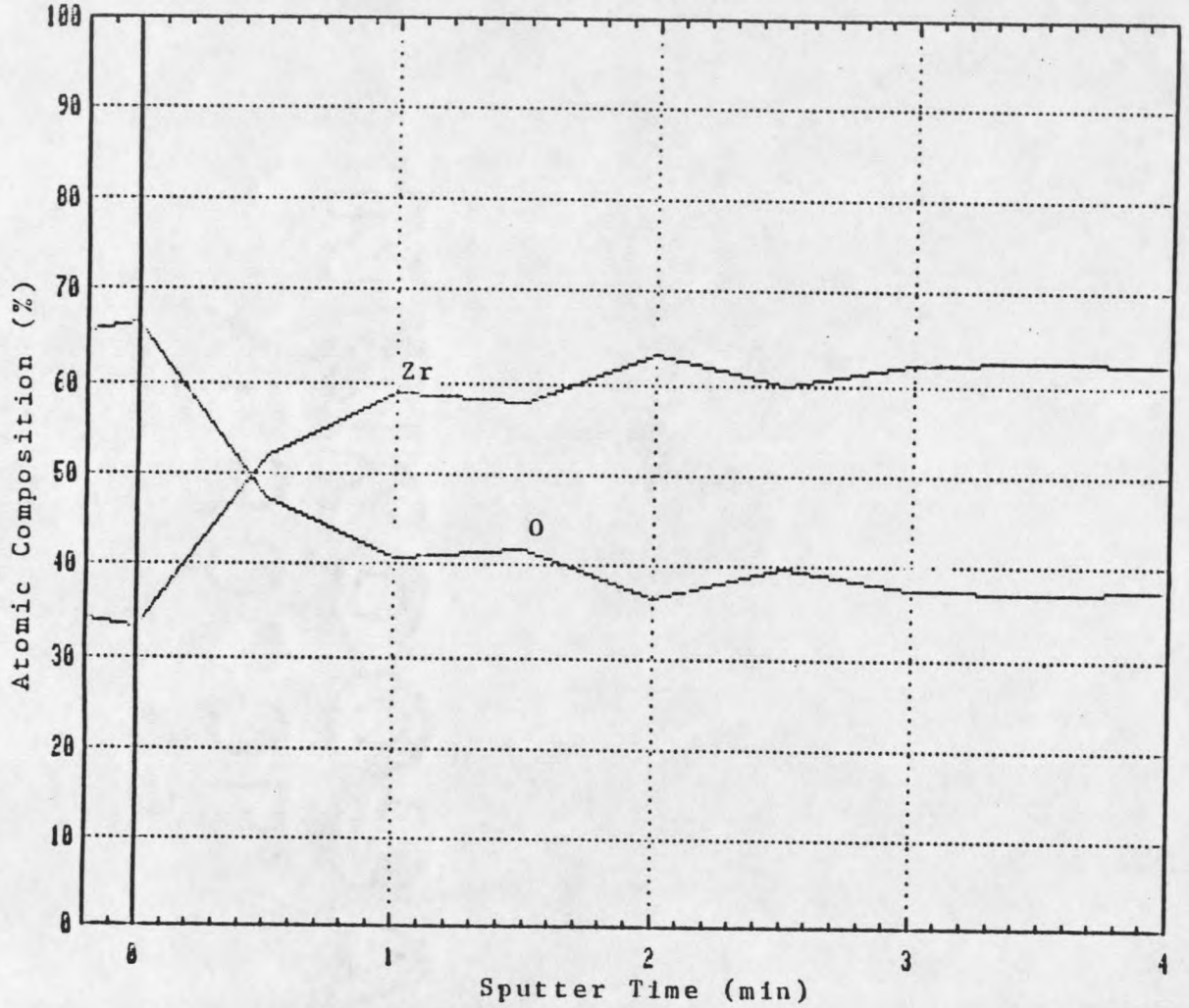

Figure 9. The compositional depth profile of Zr:Oss after 300 L O_2 exposure at room temperature

Effect of Oxidation Temperature on Surface Oxygen Concentration and Surface Oxide Layer Thickness of 300 L O_2 Exposed Zr:Oss

Figure 10 shows the AES spectra from 78 eV to 178 eV for Zr:Oss after 300 L O_2 exposure at each of several temperatures between 300 K and 1200 K. The sample was cooled in vacuum after each oxidation at temperatures above 300 K. The surface oxygen concentrations and the thickness of the surface ZrO_2 layers, established by depth profiling of the oxidized Zr:Oss surfaces, are presented in Table 1. Figure 11 shows the plot of atomic oxygen concentration vs. sputter time for each case.

The surface oxygen concentration values in Table 1 indicate the formation of a partially reduced outer surface upon oxidation and subsequent evacuation at high temperatures, especially at or above 900 K. The only exception is at 1100 K, where the surface is more oxidized than at 900 K or 1200 K. (Note: The data taken after 1100 K oxidation may not be reproducible.) This surface reduction is also indicated by the shift of the 85 eV, 110 eV and 138 eV peaks in Figure 10 to higher energies following oxidation and evacuation at sequentially higher temperatures, with the exception again of spectrum after the 1100 K oxidation. This shift in the energies of the Zr peaks brings them closer to the peak energies characteristic of

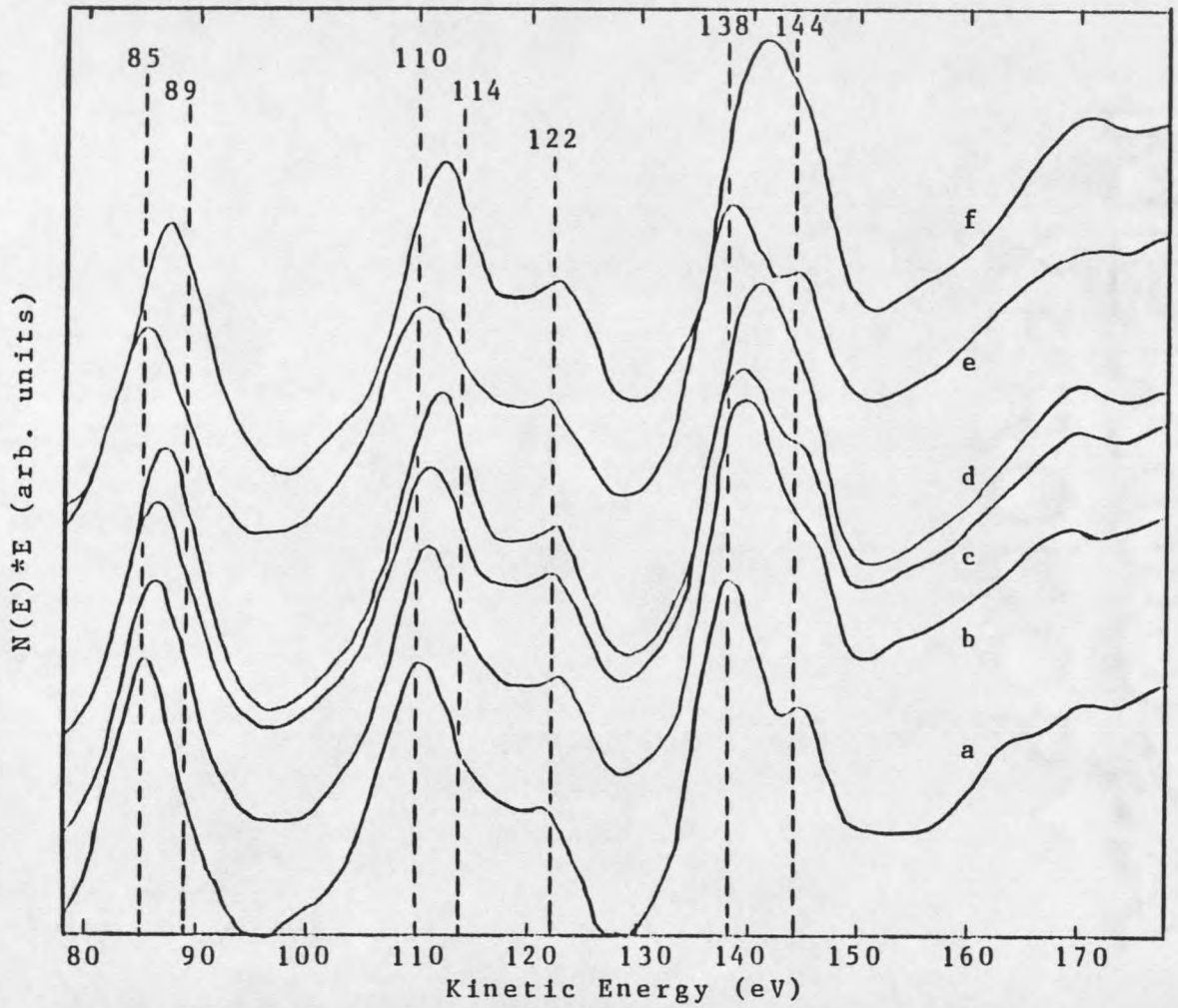

Figure 10. The AES spectra from 78 eV to 178 eV for Zr:Oss after 300 L O_2 exposure at temperatures: (a) 300 K; (b) 500 K; (c) 700 K; (d) 900 K; (e) 1100 K; (f) 1200 K

Table 1. The surface oxygen concentration and the thickness of the ZrO_2 layer formed on Zr:Oss by 300 L O_2 exposure at different temperatures

300 L O_2 exposure on Zr:Oss at 1.0×10^{-6} Torr		
Exposure Temperature, K	Resulting Surface Atomic Oxygen Concentration Determined by Depth Profiling, %	The Thickness of the ZrO_2 Layer Formed, Å
300	67	0 - 35
500	63	0 - 35
700	64	100
900	56	550*
1100	64	70
1200	56	0

* This value is for the thickness of the ZrO_2 layer under the thin reduced surface.

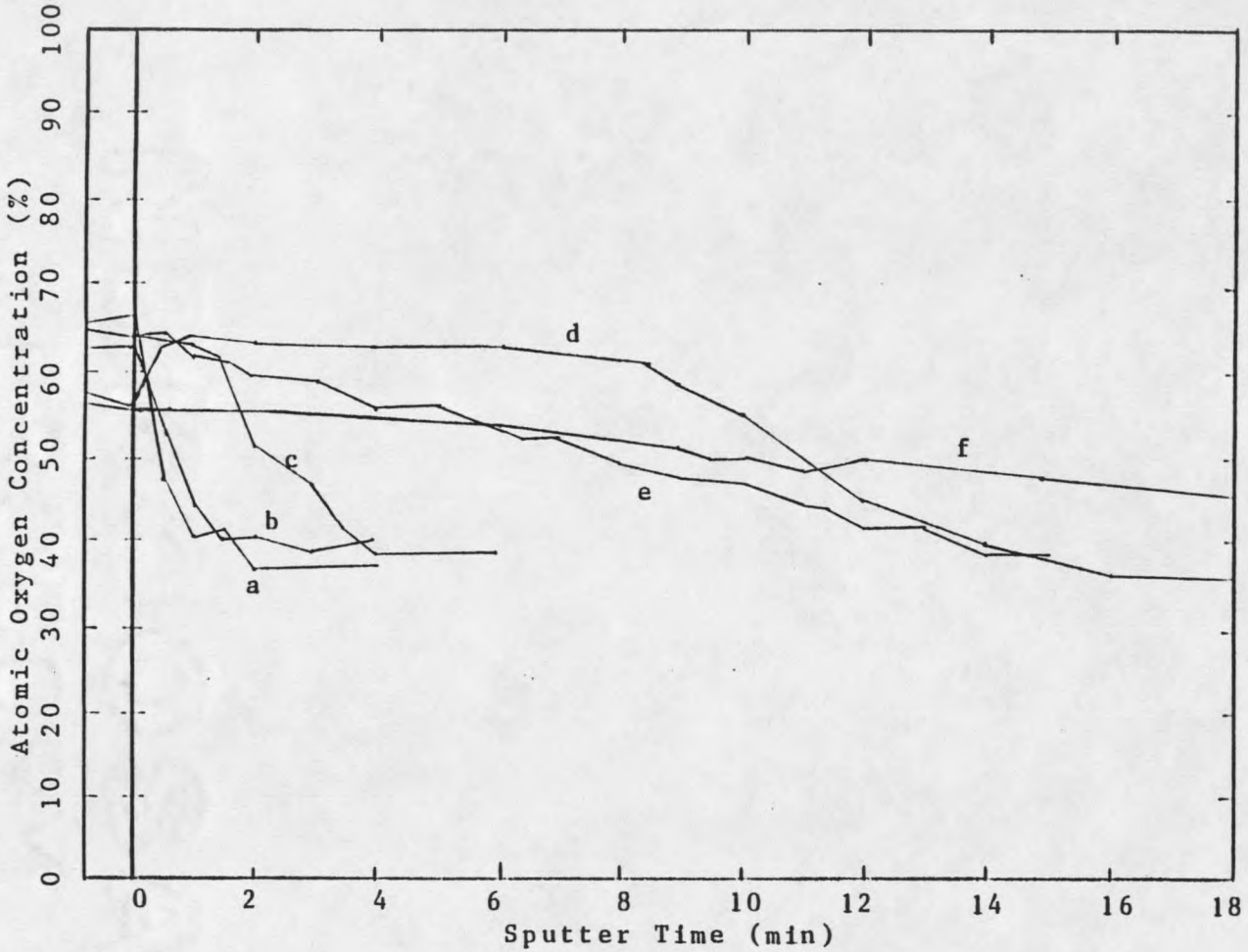

Figure 11. The depth profile of oxygen concentrations measured on Zr:Oss after 300 L O_2 exposure at temperatures: (a) 300 K; (b) 500 K; (c) 700 K; (d) 900 K; (e) 1100 K; (f) 1200 K

clean Zr, as shown in Figure 7, curve a. The depth profile for the 900 K oxidation in Figure 11 shows that under a thin reduced surface there is a ZrO_2 layer about 550 Å thick. Table 1 shows that the thickness of the ZrO_2 layer formed on Zr:Oss increases with temperature up to about 900 K and then decreases.

The AES spectrum for the 1100 K oxidation shown in Figure 10 is quite similar to the spectrum from room temperature oxidized Zr:Oss. This indicates the formation of a ZrO_2 surface upon oxidation at 1100 K. The oxygen concentration of this surface was about 64 atomic percent, which is not far from the value 67 atomic percent for ZrO_2. The small decrease in the Zr 144 eV peak intensity for the surface oxidized at 1100 K, compared to the 300 K oxidized surface, may be an indication that a thicker ZrO_2 layer was formed at 1100 K than at room temperature. As seen in Table 1, the thickness of the ZrO_2 layer formed at 1100 K is about 70 Å, which is thicker than it was at 300 K but much thinner than the ZrO_2 layer formed at 900 K.

The depth profile data in Figure 11 shows that no extended ZrO_2 layer is formed upon oxidation at 1200 K. On the other hand, the oxygen concentration profile through the bulk is much broader than from surfaces oxidized at lower temperatures. The broader oxygen concentration profile through the bulk may be an indication of the formation of

sub-oxides during oxidation at high temperatures. Many sub-oxides of Zr are known in the bulk. The highest bulk sub-oxide reported in the literature is Zr_2O [23].

Effect of High Temperature Evacuation on Zr:Oss Oxidized at 900 K with 300 L O_2

Figure 10 presents the AES spectrum from 78 eV to 178 eV for Zr:Oss cooled in vacuum after 300 L O_2 exposure at 900 K. As shown in Table 1, the surface was partially reduced, with an oxygen concentration of about 56 atomic percent. The thickness of the ZrO_2 surface under that thin reduced surface was about 550 Å. The AES depth profile conducted for this case is shown in Figure 11 and is repeated in Figure 12 together with the depth profile of Zr:Oss cooled in O_2 following 300 L O_2 exposure at 900 K.

Figure 6 shows the AES spectra from 78 eV to 178 eV for Zr:Oss cooled in 1.0×10^{-6} Torr O_2, as well as the sample cooled in vacuum, following a 300 L O_2 exposure at 900 K. The peak positions in the spectrum from the sample cooled in O_2 indicates the existence of ZrO_2 on the surface, while that of the vacuum cooled sample indicates a partial reduction of the surface. The AES depth profiles conducted on the oxidized surfaces, shown in Figure 12, indicate that the surface oxygen concentration was about 66 atomic percent

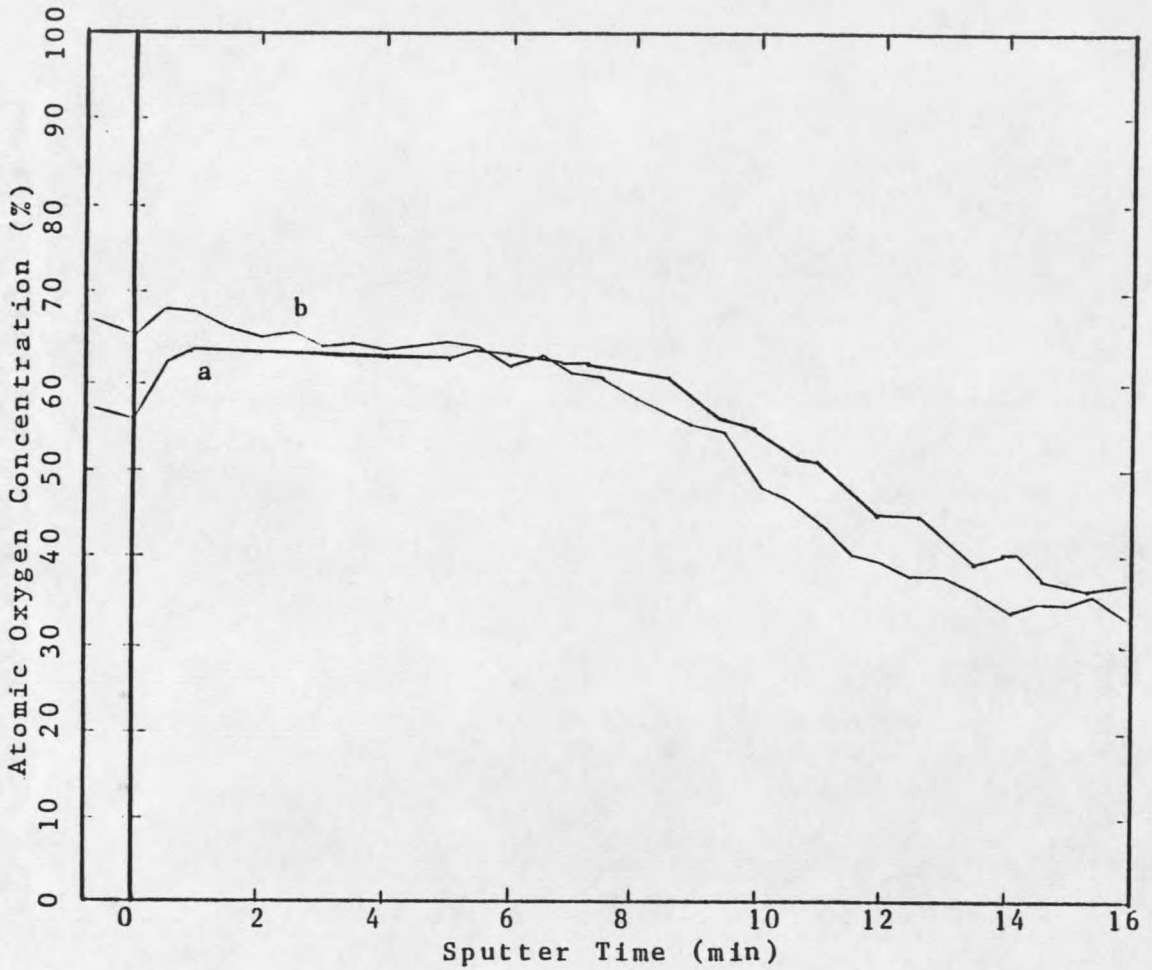

Figure 12. The AES depth profile conducted on 300 L O_2 exposed Zr:Oss at 900 K and cooled in: (a) vacuum; (b) O_2 at 1.0×10^{-6} Torr

before sputtering on the sample cooled in O_2, while it was lower for the vacuum cooled sample. The thickness of the ZrO_2 surface was determined to be about 500 Å for both samples.

The observations above indicate that the oxide layer formed on Zr:Oss at 900 K is reduced near the outermost surface if it is cooled in vacuum after the oxidation. Cooling the oxidized sample in O_2 eliminates this reduction and retains the full oxidation of the surface Zr. The thickness of the ZrO_2 layers formed on Zr:Oss are close to each other for the two cases.

Effect of High Temperature Treatment on Surface Oxygen Concentration of Zr:Oss Oxidized at 900 K with 300 L O_2 and Cooled in O_2

A Zr:Oss sample, which had been cooled in 1.0×10^{-6} Torr O_2 after a 300 L O_2 exposure at 900 K, was heat treated in vacuum at different temperatures for 5 minutes and surface analyzed by AES after cooling without conducting any depth profiling between the heat treatments. Figure 13 shows the AES spectra from 78 eV to 178 eV, which were taken after each heat treatment. The shift of the Zr AES peaks at 85, 110 and 138 eV to higher energies and the increase of the Zr 122 eV peak intensity at higher treatment temperatures are indicative of partial surface oxide reduction at high

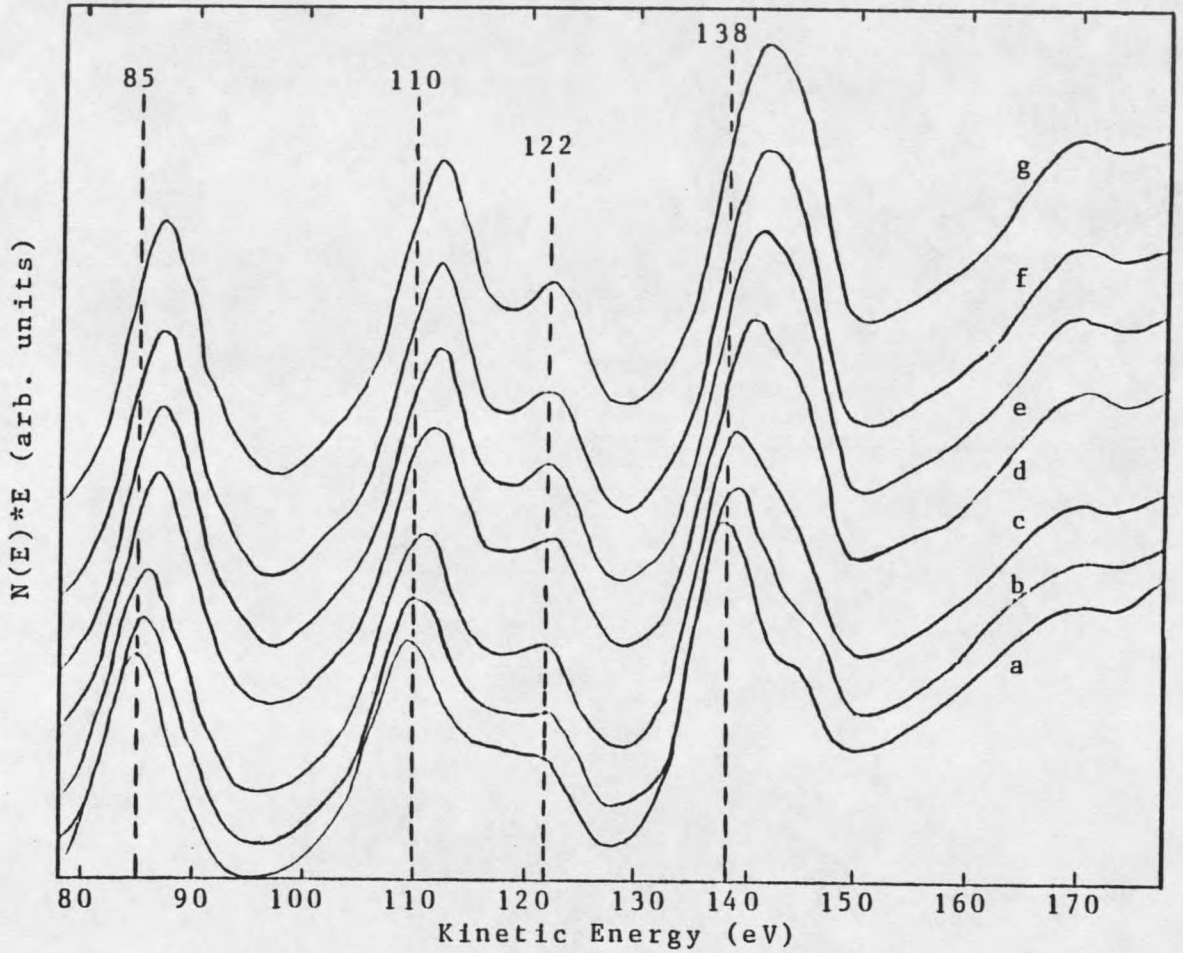

Figure 13. The AES spectra (from 78 eV to 178 eV) of a Zr:Oss sample, which had been cooled in 1.0×10^{-6} Torr O_2 after 300 L O_2 exposure at 900 K, after heat treatment for 5 min at temperatures: (a) none; (b) 500 K; (c) 700 K; (d) 800 K; (e) 900 K; (f) 1100 K; (g) 1200 K

temperatures. The resulting surface oxygen concentration after each heat treatment was determined by utilizing peak areas. The findings are summarized in Table 2. The table shows a significant decrease of the surface oxygen concentration after treatment in vacuum at high temperatures.

As another series of tests, Zr:Oss samples which had been cooled in 1.0×10^{-6} Torr O_2 following a 300 L O_2 exposure at 900 K were heat treated in vacuum at different temperatures for 5 minutes and then depth profiled. Table 3 shows the resulting surface oxygen concentration and the thickness of the surface ZrO_2 layer, determined by depth profiling after each heat treatment. The oxygen concentration profiles measured on these samples are presented in Figure 14. As can be seen in Table 3 and Figure 14, surface oxygen concentration decreases when the samples are treated at high temperatures, but there is no significant change in the thickness of the ZrO_2 layer formed on Zr:Oss.

The ZrO_2 layer formed on Zr:Oss is not significantly affected by high temperature treatments in vacuum except for the partial reduction of the outermost surface. The oxygen concentration of the outermost surface of the oxidized Zr:Oss significantly decreases at high temperatures.

Table 2. The surface oxygen concentration of a Zr:Oss sample, which had been cooled in 1.0×10^{-6} Torr O_2 after 300 L O_2 exposure at 900 K, after heat treatments at different temperatures for 5 minutes

5 Minutes Heat Treatment in vacuum at the Following Temperatures, K	The Resulting Surface Atomic Concentration Determined by Utilizing Peak Areas, %
None	67
700	65
800	60
900	54
1100	49
1200	48 (53, by Depth Profiling)

Table 3. The resulting surface oxygen concentration and the thickness of the surface ZrO_2 layer after heat treatment (at different temperatures for 5 minutes) of Zr:Oss samples which had been cooled in 1.0×10^{-6} Torr O_2 following a 300 L O_2 exposure at 900 K

5 Minutes Heat Treatment in Vacuum at the Following Temperatures, K	Surface Atomic Oxygen Concentration Determined by Depth Profiling, %	The Thickness of the ZrO_2 Layer, Å
300	66	500
700	63	620
900	58	550*
1100	58	550*

* These values are for the ZrO_2 layers under the thin reduced surfaces.

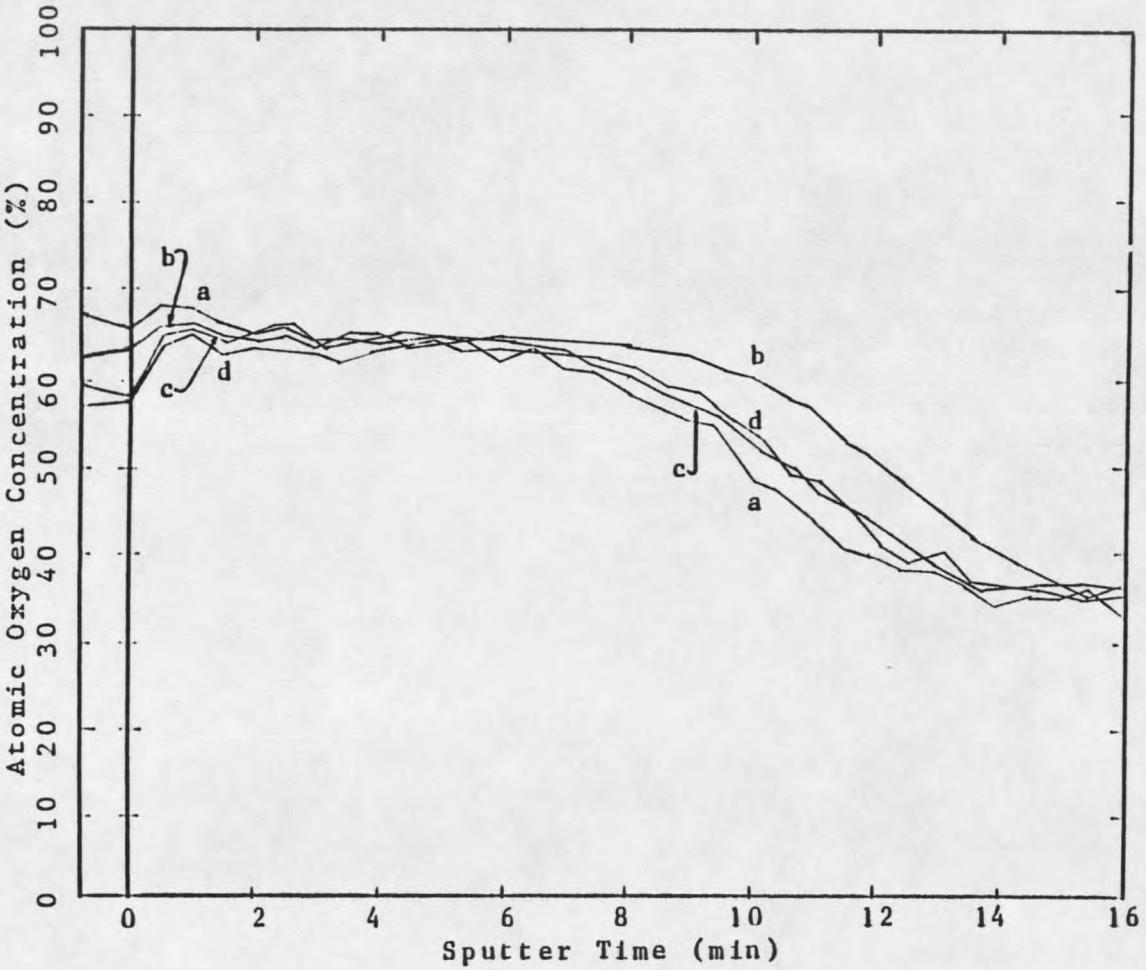

Figure 14. AES depth profiles conducted on Zr:Oss samples which had been cooled in 1.0×10^{-6} Torr O_2 following a 300 L O_2 exposure at 900 K and heat treated for 5 min at temperatures of: (a)none; (b) 700 K; (c) 900 K; (d) 1100 K

Stability of the Surface ZrO_2 Layer

Table 4 shows the surface oxygen concentrations and the thickness of the surface ZrO_2 layers determined by depth profiling of oxidized Zr:Oss samples after high temperature heat treatments in vacuum. Oxidation and heat treatment conditions are given in the table. All samples were cooled in vacuum after the initial oxidation.

The data presented in Table 4 indicate that holding an oxidized sample at 700 K in vacuum does not result in a significant change on the surface oxide formed on Zr:Oss. At temperatures of about 900 K or above, the outermost oxide surface is partially reduced but there is no significant decrease in the ZrO_2 layer thickness from dissolution into the bulk. If the substrate were not saturated with oxygen, increased oxygen diffusivity in Zr would result in oxygen permeation into the bulk metal from the surface oxide layer at measurable rates at or above 500 K [7]. Thus, the absence of a significant change of the oxide layer thickness after holding the oxidized surface at temperatures as high as 1100 K supports the assumption that the substrate used in this study was essentially saturated with oxygen. The reason for the outer surface oxide reduction at temperatures of about 900 K or above is probably the dissociation of oxygen from ZrO_2 into the vacuum at high temperatures.

Table 4. The surface oxygen concentrations and the thickness of the surface ZrO_2 layers determined by depth profiling of oxidized Zr:Oss samples after high temperature heat treatments

Oxidation Conditions*		Heat Treatment in Vacuum		Surface Oxygen Atomic Conc., %	Thickness of the ZrO_2 Layer, Å
Temp., K	O_2, L	Temp., K	Time, min		
700	300	---	None	64	100
700	300	700	60	64	100
700	300	900	5	58	100**
900	300	---	None	56	550**
900	300	900	60	56	550**
900	300	1100	5	53	550**

* The sample was cooled in vacuum after the high temperature oxidations.

** These values are for the ZrO_2 layers under the thin reduced surfaces.

Effect of O_2 Exposure Conditions on Surface Oxidation of Zr:Oss at 900 K

The surface oxygen concentration and the thickness of the ZrO_2 layer formed on Zr:Oss at 900 K for several different O_2 exposure time-pressure conditions are shown in Table 5. The samples were cooled in vacuum after oxidation.

As the data in Table 5 indicate, O_2 exposure pressure affects the surface oxidation significantly. The same O_2 exposure level which forms a ZrO_2 surface at one pressure results in a partially reduced surface at a lower exposure pressure. On the other hand, O_2 pressure does not have a significant effect on the thickness of the ZrO_2 layer formed on Zr:Oss, except at the exposure level of 30 L.

Effect of Sputtering on Surface Condition

The Zr:Oss sample which had been oxidized at 900 K and heat treated at 1200 K for 5 minutes indicated a partial reduction of the surface oxide according to its AES spectrum in Figure 13. Its surface oxygen concentration was about 53 atomic percent as shown in Table 2. This sample was sputter-cleaned for 150 seconds until a surface oxygen concentration of about 64 atomic percent was established by depth profiling. An AES spectrum taken on the sputter exposed surface is shown in Figure 15. The existence of the 138 eV

Table 5. The effect of O_2 pressure and the level of O_2 exposure on the surface oxidation of Zr:Oss at 900 K

Oxygen Exposure at 900 K			
Oxygen Exposure Level, L	Oxygen Exposure Pressure, Torr	Surface Oxygen Atomic Concentration Determined by Depth Profiling, %	The Thickness of the ZrO_2 Layer Formed, Å
30	1.0×10^{-7}	55	0
30	1.0×10^{-6}	67	0 - 35
100	3.3×10^{-7}	58	70*
100	1.0×10^{-6}	67	70
600	1.0×10^{-6}	57	760*
600	2.0×10^{-6}	66	740

* These thickness values are for the ZrO_2 layers under the thin reduced surfaces.

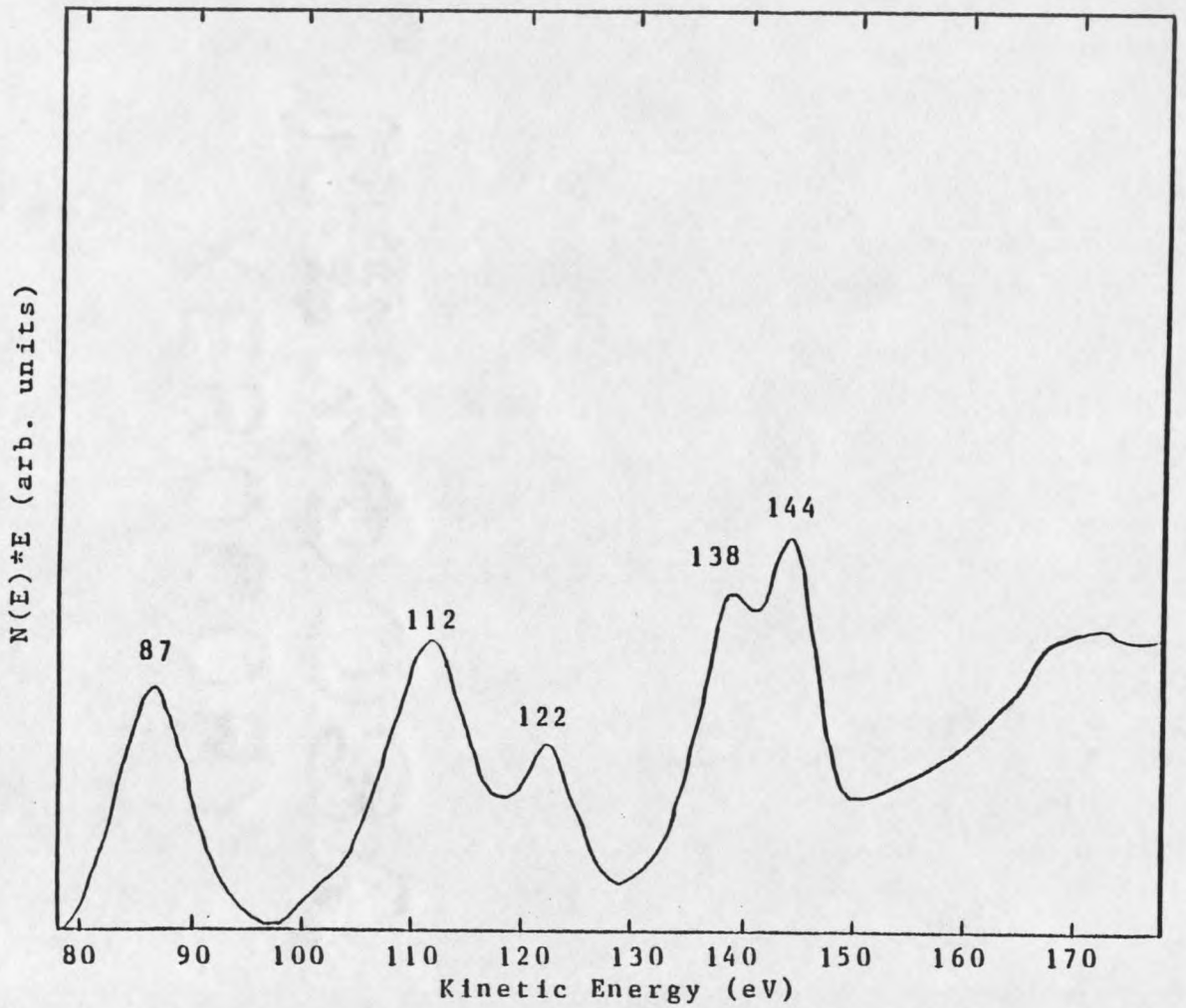

Figure 15. The AES spectrum from 78 eV to 178 eV for a sputtered ZrO_2 surface which had an oxygen concentration of about 64 atomic percent determined by using Equation 1

peak and the shifts of the Zr MNN peaks (at about 87 and 112 eV) by -2 eV, relative to clean Zr, indicate that the surface Zr is somewhat oxidized, whereas the Zr MNV peaks at 122 and 144 eV indicate the extensive presence of reduced Zr on the surface. The Zr MVV peak intensity at about 172 eV is relatively low. The AES spectrum taken after sputtering the surface for 30 more seconds was not significantly different than the spectrum shown in Figure 15 while the intensity of the oxygen AES peak at 506 eV remained high. The depth profile atomic concentration analysis indicated that there was approximately 64 atomic percent oxygen on the surface.

The reason behind the observation of a reduction of the surface Zr while the surface oxygen concentration remains high may be that the surface is disturbed by Ar^+ ions during sputtering. Ar^+ ion bombardment may result in the partial reduction of the oxidized Zr atoms on the outermost surface. One reason for the observed high oxygen concentration may be that the oxygen 506 eV Auger transition escape depth includes both the reduced outermost surface and the oxide layer under that disturbed surface, whereas the Zr 89 eV Auger transition arises from a shallower depth. The escape depth is about 5.9 Å for the Zr peak at 89 eV. This is shallower than the escape depth of about 13 Å for oxygen Auger transition at 506 eV [20].

Relation of Observed High Temperature Surface Reduction to Catalytic Mechanisms on ZrO_2

Studies of the catalytic mechanism of CH_3OH formation on ZrO_2 by Ekerdt and Jackson [24] indicate that the surface reaction steps depicted in Figure 16 are followed. This proposed mechanism postulates the formation of carbonate, formate, and methoxide surface species in the hydrogenation of CO on ZrO_2. Surface hydrogen, hydroxyl, water groups, and partially reduced zirconium are involved in the surface reaction sequence [2,3,4,24].

The results of this study provide support for the mechanism for methanol synthesis over ZrO_2 proposed by Ekerdt and Jackson. They demonstrated that ZrO_2 is an active catalyst for CO reduction by H_2 at about 973 K. The reducing environment present in the H_2, CO reaction system would most probably support the formation of a partially reduced ZrO_2 surface, very much like that observed in this research at or above about 900 K. The demonstration of partially reduced ZrO_2 surfaces in vacuum at high temperatures therefore provides direct evidence of the existence of the partially reduced Zr on ZrO_2, which is required in the proposed reaction mechanism.

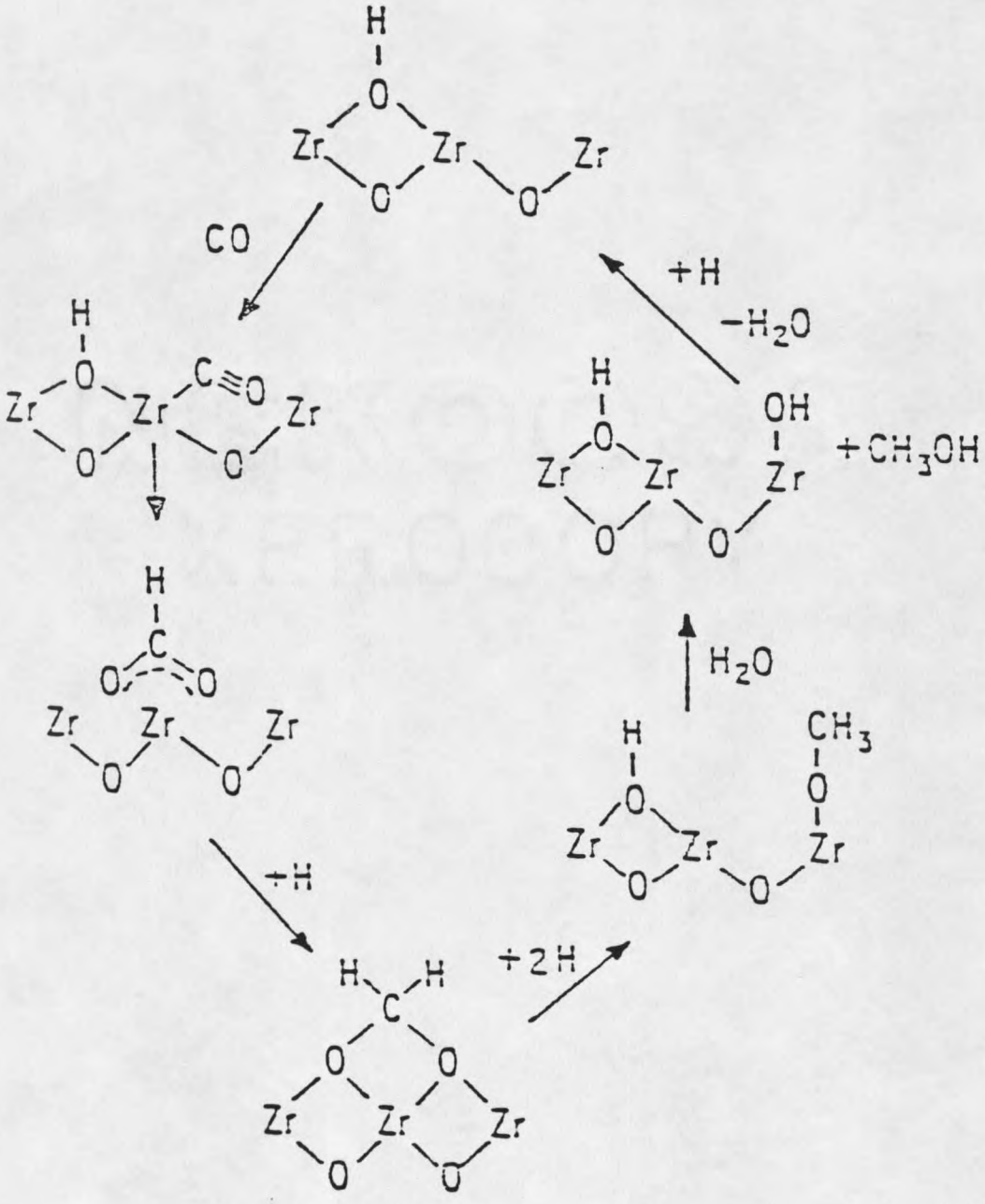

Figure 16. Proposed mechanism for methanol synthesis over ZrO_2 [24]

SUMMARY AND CONCLUSIONS

The objective of this research was to develop and characterize a model ZrO_2 test catalyst surface on a conductive substrate, which can be directly tested by high vacuum electron and ion spectroscopic methods which require some mode of surface charge dissipation during testing. The significant findings of this investigation are as follows:

1. It is possible to form a thin ZrO_2 surface layer on a conductive oxygen-saturated zirconium metal substrate which provides for the dissipation of surface electrical charge during spectroscopic surface studies.

2. The thickness of the ZrO_2 surface layer formed increases with O_2 exposure temperature up to about 900 K and then decreases.

3. The oxide layer formed at 900 K is reduced near the outermost surface if it is cooled in vacuum after the oxidation. This reduction may be eliminated by cooling the oxidized sample in O_2, as this retains the full oxidation of the surface Zr.

4. For oxidation temperatures above 900 K, the oxygen

concentration profiles indicate lower oxygen concentrations through the surface oxide layer compared to surfaces oxidized at 900 K or lower. The surface oxide layers formed at temperatures above 900 K also extend further into the Zr:Oss substrate than those formed at 900 K. This may indicate the formation of sub-oxides of Zr upon oxidation at temperatures above 900 K.

5. The ZrO_2 surfaces formed are stable at temperatures up to about 900 K. The outermost surface becomes reduced at or above 900 K, but the oxide layer under that thin reduced surface stays stable at even higher temperatures. The highest temperature tested was 1200 K.

6. Sputtering the ZrO_2 surface layer with argon ions produces a partially reduced Zr surface.

RECOMMENDATIONS

Based on the results of this experimental work, the following recommendations are made:

1. Extended AES studies of the oxidation of oxygen-saturated zirconium (Zr:Oss) at 900 K at various oxygen exposures and pressures would provide more information about the pressure effect on the surface oxidation of Zr:Oss at this temperature.

2. If this type of ZrO_2 surface is utilized in an investigation of the catalytic properties of ZrO_2, it should be formed on a Zr:Oss substrate at temperatures lower than about 900 K or the sample should be cooled in O_2 after oxidation at 900 K. The temperature of the oxidized sample should not pass about 900 K if the surface reduction will be any problem for the catalytic investigation.

3. The surface of bulk ZrO_2 should be investigated for evidence of surface Zr reduction at high temperatures.

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APPENDIX

The difference in Zr atom density in Zr and ZrO_2

Atomic density of Zr = [density* of Zr/atomic weight of Zr] x Avagadro's number

= [6.49 (g/cm^3) / 91.22 (g/gmol)]

x 6.02×10^{23} (atoms/gmol)

= 4.28×10^{22} atoms/cm^3

Molecular dens. of ZrO_2 = [dens.* of ZrO_2/mol. wt. of ZrO_2] x Avagadro's number

= [5.89 (g/cm^3) / 123.22 (g/gmol)]

x 6.02×10^{23} (molecules/gmol)

= 2.88×10^{22} molecules/cm^3

1 ZrO_2 molecule has 1 Zr atom in it. Hence, Zr atom density in ZrO_2 is the same as the molecular density of ZrO_2. That is:

Zr atom density in ZrO_2 = 2.88×10^{22} atoms/cm^3

The difference in Zr atom density in Zr and ZrO_2 = $(2.88 \times 10^{22}/4.28 \times 10^{22}) \times 100$ = 67 %

* Density values, which are at room temperature, were taken from Reference [25].

Note: dens. = density, and mol. wt. = molecular weight