Initial Stages of Oxide Formation on Rhodium Field Emitters

G. L. Kellogg

Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 4 September 1984)

The nucleation and growth stage of oxide formation on Rh field emitters has been investigated by imaging atom-probe mass spectroscopy. Quantitative atom-probe analysis of samples heated in 1-Torr O_2 indicated that stoichiometric Rh_2O_3 is formed at temperatures as low as 500 K and suboxides are formed at lower temperatures. The activation energy for the process was determined from the temperature dependence of the surface oxygen accumulation rate to be 4–5 kcal/mole.

The oxidation of metal surfaces typically occurs in three stages: Oxygen adsorbs from the gas phase; an oxide nucleates and grows until an oxide film covers the surface; and the oxide increases its thickness by solid-state diffusion of the reactants through the film.[1] For noble metals, the most difficult stage of the process to investigate is the nucleation and growth stage[1] because experiments typically require the use of relatively high pressures for oxidation and ultrahigh vacuum conditions for analysis. In this paper we report an investigation of the early stages of oxide growth on rhodium field-emitter surfaces. An ultrahigh-vacuum, sample-transfer system was employed to overcome the pressure differential problem, and the oxidation process was characterized by imaging atom-probe mass spectroscopy.[2] The conditions of temperature and oxygen pressure required to produce stoichiometric Rh_2O_3 were determined, and an activation energy for the initial stages of oxidation was measured for the first time.

The choice of rhodium for the substrate was motivated by its well-known catalytic properties.[3] The catalytic efficiency obviously depends on the surface properties of the catalyst, and, for some reactions, it is believed that the oxidation of the surface actually poisons the reaction.[4,5] The study reported here was undertaken to characterize the oxidation process in pure O_2 to serve as a basis for studies of the oxidation of the surface during catalytic reactions.[6] The use of a field-emitter sample is advantageous in this respect because its surface closely resembles that of a typical catalyst particle.

The atom-probe field-ion microscope and imaging atom probe have been previously employed to study the oxidation of Ru[7] and Pt-Rh alloy[8] samples. Information on the structure and chemical form of the oxides as well as the oxide-metal interfaces was obtained. The present study differs from the earlier work in that here the amount and chemical composition of the oxide was determined as a function of oxidizing conditions, and the very early stages of oxide growth were examined.

The apparatus used in this study consisted of two chambers: a reaction chamber where the oxidation ex-

periments were conducted and an analysis chamber where the sample surface was examined. The rhodium samples (called field emitters or tips) were transferred between the two chambers on a stainless-steel rod magnetically coupled to the exterior of the vacuum system. The tips were prepared from 0.005-in.-diam polycrystalline Rh wire by electropolishing them in a molten $NaNO_3$-NaCl solution.[9] This procedure produces both $\langle 111 \rangle$ and $\langle 100 \rangle$ oriented tips; however, only tips with a $\langle 100 \rangle$ orientation were used in this study. The sample tips were spotwelded to a wire loop of 0.005-in.-diam Pt, which served as both a support and a heating element. The tips were introduced into the vacuum system through the reaction chamber and transferred to the analysis chamber for final surface preparation. The surfaces were cleaned with a combination of neon cathode sputtering[10] and field evaporation.[9] The cathode-sputtering technique was used to remove contamination from the tip shank, and field evaporation was used to remove the damage resulting from the sputtering process and to clean the tip apex. Both procedures were performed in UHV with the sample at room temperature.

Following the cleaning in the analysis chamber, the tip was retracted into the reaction chamber, and the oxidation experiments were initiated. Spectroscopic-grade oxygen was admitted to the chamber at a pressure of 1 Torr. The sample was heated to temperatures between 350 and 550 K, temperatures well below the dissociation temperature of the oxide at 1 Torr. The tip was heated by a dc current through the Pt support loop, and the temperature was determined by resistivity measurements.[11] Absolute temperatures were accurate to within ± 10 K, and relative temperatures to within ± 1 K. After a 15-min interval, the heating was terminated and the oxygen pumped out. When the pressure in the reaction chamber reached the low-10^{-7}-Torr range, the sample tip was transferred back to the analysis chamber, and the surface was examined by imaging atom-probe mass spectroscopy.

The imaging atom-probe technique, which has been described in detail by Panitz,[12] is used to probe the chemical composition of the tip surface. A dc holding

© 1985 The American Physical Society

voltage and a high-voltage electrical pulse are applied to the tip such that the sum of the two voltages produces field strengths sufficient to field desorb surface species as positive ions. The desorbed ions travel across a field-free region and are detected by a set of channel-plate ion detectors. The mass-to-charge ratios of the desorbed species are determined by their flight times, which are measured on the sweep of a fast transient wave-form digitizer. Figure 1 shows an example of a digitizer trace, which we refer to as our imaging atom-probe mass spectrum. This mass spectrum was taken from a Rh sample after it had been heated in 1 Torr of O_2 at 500 K for 15 min. The trace consists of a series of peaks, and these peaks identify the desorbed surface species. The amplitude of each peak is proportional to the number of ions of the given species desorbed. A procedure for converting peak amplitudes to the actual number of ions desorbed has recently been developed,[11] and we have applied this procedure to rhodium and oxygen ions. In the mass spectrum shown in Fig. 1 the conversion is 6 ± 1 ions/mV. Thus, each mass spectrum contains information on the abundance of the different species desorbed.

Our analysis of the oxidized Rh surfaces consisted of recording a series of mass spectra beginning at a dc voltage where species were first detected and continuing until only bulk Rh was detected. The atom-probe analysis was performed with the sample at room temperature. In a typical experiment, 20–30 individual mass spectra such as the one shown in Fig. 1 were recorded; this represents a total of tens of thousands of ions detected. The species detected in Fig. 1 strongly suggest that a surface oxide has been formed at 500 K. However, the composition of the oxide is not evident. This information can be obtained by the plotting
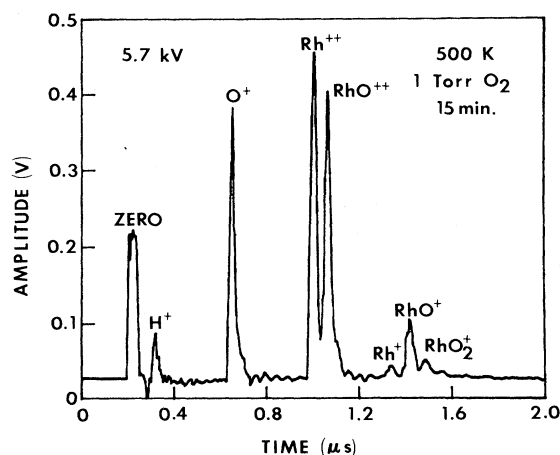
of the cumulative number of oxygen atoms versus the cumulative number of rhodium atoms for successive mass spectra. The cumulative number of oxygen atoms is obtained by addition of O^+, RhO^{++}, RhO^+, and twice the RhO_2^+ signals and multiplication by the above conversion factor. The cumulative rhodium atoms are obtained in a similar manner. Since the oxide desorbs at fields lower than the evaporation field of Rh, the initial slope of the plot gives the chemical composition of the oxide. As the oxide is removed, the plot saturates at a value proportional to the total amount of accumulated oxygen.

In order to remove the entire oxide layer by field desorption, the field must be increased to the point where field evaporation of the substrate may also occur. With consideration of the large surface area analyzed with the imaging atom probe, it is likely that the oxide in low-field regions and the substrate in high-field regions desorb simultaneously as the interface is approached. Thus, the composition of the oxide at the interfacial region cannot be determined from our cumulative plots. To obtain this information a much smaller region must be probed.[7]

A series of cumulative plots taken from a sample heated to various temperatures in 1-Torr O_2 for 15 min is shown in Fig. 2. The initial $\frac{3}{2}$ slope of the plots corresponding to 500 and 550 K indicates that stoichiometric Rh_2O_3 was formed under these conditions. This result at 500 K was reproducible over eight experiments on three different samples. At lower temperatures, however, lesser slopes were obtained, which indicated that the oxides were not fully stoichiometric. The trend, evident in Fig. 2, was that the lower the temperature, the lower is the oxygen content of the oxide. These "suboxides" could be actual non-
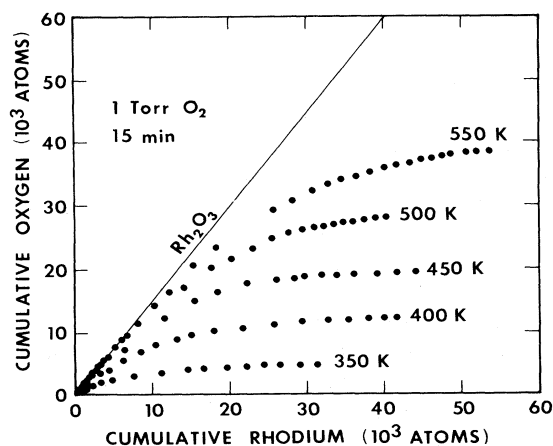

FIG. 1. An imaging atom-probe mass spectrum taken from a rhodium sample after heating to 500 K in 1 Torr of O_2. The four major peaks indicate that an oxide has been formed.

FIG. 2. A series of cumulative plots taken following heating in 1 Torr O_2 at various temperatures. Stoichiometric Rh_2O_3 is formed at temperatures of 500 K and above. The total amount of accumulated oxygen increases with temperature.

stoichiometric oxides or simply dissolved oxygen of various concentrations. With use of the technique as described, the distinction could not be made. The above results, however, have identified the conditions required to produce a stoichiometric oxide on Rh. Field-ion microscopy of the oxide, which will be discussed in detail elsewhere, indicated that the oxide formed at 500 K was, at most, several layers thick above the (100) plane and grew preferentially at the steps of the surface.

The total amount of accumulated oxygen was also found to be a strong function of temperature. The saturation values of the cumulative plots shown in Fig. 2, which reflect the total accumulated oxygen, increase significantly as a function of temperature. Strictly speaking, the saturation values cannot be associated with an oxidation rate because the chemical form of the oxide varies as a function of temperature. However, the saturation values are proportional to an oxygen accumulation rate (regardless of the oxide produced), as long as the accumulation rate is constant over the 15-min heating intervals. Preliminary studies of the saturation values versus time indicate that the accumulation rate is constant, which allows us to plot the saturation values as a function of temperature in Arrhenius form and obtain an activation energy for the process. Such a plot is shown in Fig. 3. The linearity of the plot indicates that the accumulation of oxygen is a thermally activated process; the slope yields an activation energy of 4.0 kcal/mole. The accuracy of the data was checked by repetition of the experiment at 500 K nine times. The standard deviation of the mean from these nine experiments was less than 10% of the average value plotted in Fig. 3. Also, the entire experiment was repeated on a separate sample at temperatures between 400 and 600 K. A similar Arrhenius plot yielded an activation energy of 5.0 kcal/mole.

The similarity between measured activation energy and the activation energy for dissociation of O_2 on Rh(100) [13] initially led us to conclude that oxygen dissociation was the rate-determining step in the initial stages of the oxidation process. However, under these conditions of temperature and O_2 pressure it is highly probable that the surface is covered with dissociated oxygen, and the 4–5-kcal/mole activation energy is more likely associated with the dissolution of oxygen into the bulk, surface rearrangement processes, or the migration of oxygen atoms to nucleation sites. From the present study, it is not possible to distinguish between these possibilities. For any of these processes, the rate is independent of the oxide eventually formed and one is still justified in associating our accumulation rate with the overall oxidation rate. It is expected that the measured activation energy will be applicable for oxidization up to the point where the surface is fully oxidized and then another growth mecha-
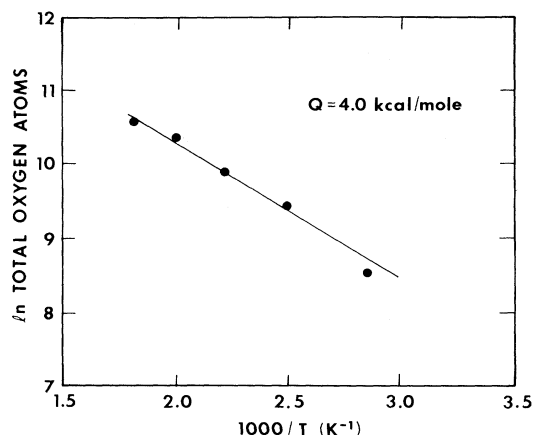

FIG. 3. An Arrhenius plot of the saturation values from Fig. 2. The linearity of the plot indicates that the process is thermally activated, and the slope yields an activation energy of 4.0 kcal/mole.

nism will take over.

Controlled oxidation of the single-crystal Rh(111) surface has been previously investigated by low-energy-electron diffraction and Auger-electron spectroscopy. [14] Since the primary focus of the single-crystal studies was to characterize all stages of oxide growth, high-pressure oxidation of the surface was not systematically examined as a function of temperature. However, it was reported that epitaxial Rh_2O_3 grows upon heating in 1-Torr O_2 at 975 K, a result consistent with the conditions required for oxidation reported here.

In summary, Rh field emitters were heated in 1 Torr of O_2 at temperatures between 350 and 550 K, and their surfaces were subsequently analyzed by imaging atom-probe mass spectroscopy. Stoichiometric Rh_2O_3 was produced at temperatures as low as 500 K and nonstoichiometric oxides were formed at lower temperatures. The activation energy for the accumulation of oxygen was measured to be 4–5 kcal/mole, which is significantly lower than the activation energy for the growth of bulk oxide. Further studies of the time and temperature dependence of oxide formation are in progress and are expected to provide more detailed information on the energetics and kinetics of the oxidation process.

[1]See, for example, Per Kofstad, High Temperature Oxidation of Metals (Wiley, New York, 1966).

[2]J. A. Panitz, Rev. Sci. Instrum. **44**, 1043 (1973).

[3]See, for example, J. T. Yates, Jr., P. A. Thiel, and W. H. Weinberg, Surf. Sci. **82**, 45 (1979), and references therein.

[4]S. H. Oh and J. E. Carpenter, J. Catal. **80**, 472 (1983).

[5]G. B. Fisher and D. W. Goodman, private communication.

[6]G. L. Kellogg, to be published.

[7]G. K. L. Cranstoun, D. R. Pyke, and G. D. W. Smith, Appl. Surf. Sci. **2**, 375 (1979).

[8]A. R. McCabe and G. D. W. Smith, in *Proceedings of the Twenty Ninth International Field Emission Symposium,* edited by H.-O. Andren and H. Norden (Almqvist & Wiksells, Stockholm, 1982), p. 201.

[9]E. W. Müller and T. T. Tsong, *Field Ion Microscopy, Principles and Applications* (Elsevier, New York, 1969).

[10]G. K. L. Cranstoun, D. J. Browning, and D. R. Pyke, Surf. Sci. **34**, 597 (1973).

[11]G. L. Kellogg, Phys. Rev. B **29**, 4304 (1984).

[12]J. A. Panitz, *Progress in Surface Science,* edited by S. G. Davison (Pergamon, New York, 1973), Vol. 8, Part 6.

[13]Galen B. Fisher and Steven J. Schmieg, J. Vac. Sci. Technol. A **1**, 1064 (1983).

[14]D. G. Castner and G. A. Somorjai, Appl. Surf. Sci. **6**, 29 (1980).