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THE STUDY OF RUTHENIUM OXIDATION BY PULSED FIELD DESORPTION MASS SPECTROMETRY


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Résumé - Les intermédiaires de surface impliqués dans l'oxydation du Ru à 700 K ont été examinés par spectrométrie de masse de désorption de champ pulsé. Les résultats sont comparés avec ceux obtenus par SMIS, spectrométrie de masse de sonde atomique et spectrométrie de masse d'évaporation thermique. Des ions chargés simples et doubles de Ru, RuO, RuO₂ et RuO₃ aussi bien que Ru₂O²⁺ et Ru₂O₃⁺, sont observées. La présence d'une couche préoxydée sur la pointe de Ru s'est avérée être nécessaire avant le formation de RuO₃ apparaisse. RuO₃ était formé pour une température supérieure à 600 K à 10⁻³ Pa O₂. À 600 K, une haute mobilité des espèces d'oxyde a été observée.

Abstract - The surface intermediates involved in the oxidation of ruthenium at 700 K were examined by pulsed field desorption mass spectrometry (PFDSMS). The results were compared with those from SIMS, atom probe and thermal vaporization mass spectrometry. Singly and doubly charged ions of Ru, RuO, RuO₂, and RuO₃ as well as Ru₂O²⁺ and Ru₂O₃⁺ were observed. The presence of a pre-oxidized layer on the ruthenium tip was found to be necessary before any RuO₃ formation occurred. RuO₃ was formed at temperatures above 600 K at 10⁻³ Pa O₂. At 600 K, the oxide species were observed to be highly mobile.

I - INTRODUCTION

The chemisorption of oxygen on ruthenium has been extensively studied with various surface sensitive techniques /1/. However, little is known about the oxidation at high temperatures. This is surprising in view of the great importance of the metal for applications in catalysis. The practical use is limited because of the tendency of the metal to form volatile oxides, RuO₃ and RuO₄. Kim and Vinograd /2/ used XPS and found that RuO₃ may be present as a defect structure of RuO₂. Thermal desorption...
spectra of oxygen from ruthenium contained features which are possibly related to surface oxides or their precursors which release oxygen /3/. Cranstoun et al. /4,5/ performed studies on the oxidized metal by means of field ion microscopy and atom probe time-of-flight mass spectrometry. The authors identified a film of RuO$_2$ of several ten layer thickness as a crystalline oxide. In addition, O$^+$ and RuO$_{2x}^{2+}$ ions (x=1...3) have been detected.

In contrast to this, SIMS analysis of the oxide between 300 and 700 K yielded O$_2^+$, RuO$^+$, and Ru$_3$O$^+$ ions /6/.

In order to examine the intermediate stages of oxide formation we employed pulsed field desorption mass spectrometry (PFDMS). This method has already been used in studies of metal oxidation /7/.

**II - EXPERIMENTAL**

The implications of the PFDMS technique for studying the kinetics of chemical reactions at surfaces have been described in detail elsewhere /8,9/. Fast negative pulses (up to 20 kV amplitude, a few 100 ns width, repetition rates up to 100 kHz) are applied to a counter electrode in front of a ruthenium field emitter tip. The field pulses desorb the particles, adsorbed at the emitter surface, in a controlled manner. The respective ions are chemically analyzed by time-of-flight mass spectrometry. The Ru tip was spark erosion cut from a boule supplied by Materials Research Corporation, and electrolytically etched. Cleaning of the tip surface could be achieved in situ by field evaporation.

**III - RESULTS AND DISCUSSION**

For the measurements, to be reported here, we pretreated the Ru field emitter in situ with oxygen at 900 K, 1.3 x 10$^{-2}$ Pa, at least 2 hours.

After cooling down to 700 K, field desorption under dynamic oxygen supply at 1.3 x 10$^{-3}$ Pa yielded mass spectra which contained various kinds of singly and doubly charged ions. Besides the field evaporated Ru$^{n+}$ ions, we detected Ru$_x$O$_y$$^{n+}$ up to ruthenium trioxide and its dimer. The RuO$_{2n}^{n+}$ ions originate from the tightly bound oxide layer as well as from more weakly bound RuO$_2$ molecules, as will be discussed below.

The formation of an oxide phase was also observed by Cranstoun et al. /4/ under oxygen treatment at 900 K.

The dependence of the ion intensities on the (pulsed) desorption field strength is shown in fig. 1. The intensities of RuO$^{n+}$, Ru$_2$O$^{n+}$ and Ru$_3$O$^{n+}$ have been summed up as suboxide species. According to the different field strength dependence we distinguish suboxides, molecular ions (RuO$_2^+$ and RuO$_3^+$), and cluster ions (Ru$_2$O$_4^+$, Ru$_2$O$_5^+$, Ru$_2$O$_6^+$). At low field strengths, the molecular ions dominate. They appear considerably below the onsets of the clusters and the suboxides. Thus we conclude that both
RuO$_2^+$ and RuO$_3^+$ originate from rather weakly bound molecules. At high field strengths, RuO$_2^+$ increases continuously, whereas the RuO$_3^+$ intensity peaks at a moderate field strength, and decreases further on. The cluster ions Ru$_2$O$_4^+$, Ru$_2$O$_5^+$, and Ru$_2$O$_6^+$ behave in a similar manner as RuO$_3^+$, i.e. their intensities first increase due to an increasing ionization probability, pass a maximum and then decrease. This intensity decrease coincides with the sharp onset of the suboxide ions. Due to

![Image of graph showing variation of pulsed desorption field strength. Oxide ions with less than two oxygen atoms per ruthenium atom are summed up. The calibration of the field strength scale is not very accurate. Conditions: Tip temperature 700 K, oxygen pressure 1.3 x 10$^{-3}$ Pa, monitored area 2 nm$^2$, (0001) oriented; desorption pulse width 300 ns; reaction time between pulses 100 us.]

the removal of oxygen containing particles from the surface (by the field pulses),
The oxidation state of the oxide layer is considerably lowered at the highest field strengths.

The high intensities of the suboxide ions and the $\text{RuO}_2^+$ can only partly be explained by impingement of gaseous $\text{O}_2$ and subsequent reaction with the Ru surface in the monitored area. There must be an additional supply by diffusion of surface species into the monitored area at the apex of the tip. At the shank of the emitter tip the field strength is low, so that the equilibrium oxide structure is not disturbed by the field pulses, and weakly bound RuO$_2$ and RuO$_3$ molecules are formed. Along the path from the shank to the apex the chemical potential of the oxide layer varies, so that RuO$_3$ and also possibly other oxide species, like RuO$_2$, diffuse to the apex. There, at oxygen deficient sites, they may decompose. However, the decomposition and incorporation into the oxide layer does not restore its high oxidation state, because the field pulses continuously remove oxide ions.

Further confirmation of the mobility of oxide molecules is obtained from the following observations:

- The oxide ion intensity is kept high for several minutes after removing the oxygen gas supply, by pumping down quickly below $10^{-5}$ Pa. The lower the desorption field strength, the slower the decrease of the ion intensity.
- No substantial blunting of the field emitter has been observed, although a few ten thousand ruthenium oxide ions were detected, which corresponds to several hundred layers. This observation can only be understood in terms of mobile species ensuring transport to the apex of the tip, instead of removal of lattice layers at the apex.
- Reaction time variation at a high desorption field strength reveals a steep increase of the RuO$_3$ surface concentration after a certain delay. This delay time, about 10 ms at 30 V/nm, increases at higher field strengths. It takes a longer time to restore the oxide layer, when the layer more strongly deviates from the high oxidation state. After the delay period, the intensity increases by two orders of magnitude within one order of magnitude time variation. This steepness is evidence for a diffusion supply from the shank into the monitored area, rather than for a kinetic limitation of the formation process.

The preceding discussion confirms RuO$_3$ as a mobile molecule. However, the detection of high RuO$_2^+$ intensities at low field strengths (fig. 1), and the presence of RuO$_2^+$, besides RuO$_3^+$, after removing the oxygen gas supply, support the existence of a mobile RuO$_2$ molecule. Only at higher field strengths, where suboxides are desorbed, RuO$_3$ may decompose and transfer oxygen into the oxide layer. At low field strengths, however, the high RuO$_2^+$ intensity cannot solely be explained by decomposition of RuO$_3$.

The continuous increase of the RuO$_2^+$ intensity in fig. 1 - as compared to the decreasing trend of RuO$_3^+$ - is due to an increasing desorption of RuO$_2^+$ from the more
A possible mobility of suboxide species remains an open question. Our measurements gave no indication, either for or against mobility. The existence of suboxide ions could easily be understood by decomposition of mobile RuO$_2$ and RuO$_3$ as well as reaction of the ruthenium with impinging oxygen. Both reactions seem to occur.

The behaviour of the cluster species in fig. 1 indicates that these molecules are formed in a consecutive surface reaction from mobile RuO$_2$ and RuO$_3$.

When the surface concentration of these molecules decreases at high field strengths, the concentration of the cluster species has to decrease likewise.

The existence of clusters with more than two oxygen atoms per ruthenium atom coincides with the observation of an amorphous like higher oxidation state layer by Winograd /2/. It is likely that RuO$_2$ and RuO$_3$ act as intermediate species in the reaction towards the volatile RuO$_4$ molecule. At the reaction conditions chosen for the reported measurements, no RuO$_4^+$ has been detected. However, when decreasing the surface temperature to 400…450 K at 1.3 x 10$^{-3}$ Pa oxygen pressure and low field strength, we obtained mass spectra with a considerable amount of RuO$_4^+$ (besides RuO$_2^{n+}$ and RuO$_3^{n+}$, n=1,2). The formation of the volatile RuO$_4$ molecule on a high oxidation state oxide is in accord with thermodynamic considerations. The lower temperature possibly influenced the oxidation state of the oxide layer; the main reason for the observation of RuO$_4^+$, however, is the increase of the mean lifetime of RuO$_4$ and, consequently, its concentration at the surface. Mobile molecules with high oxidation states exist on an oxidized ruthenium surface, even at low oxygen pressures. This observation confirms that the processes at the interface between bulk ruthenium and the oxide phase are rather slow, hence their rates are accessible to the pulsed field desorption technique.

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