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Secondary Ion Yields in Low Energy SIMS Experiments

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ABSTRACT

The chemisorption of oxygen on W(100) and Mo(100) single crystal surfaces were studied using a static mode SIMS technique at primary ion energies ranging from 150 eV to 2 keV. The following secondary ion yields O^- , WO_2^- , and MoO_2^- were found to be sensitive to the changes in the chemisorbed oxygen layer at different stages of chemisorption. Significant enhancement in the sensitivity of the O^- yield to the chemisorption process was observed when the energy of the Ne^+ primary ion energy was below 500 eV.

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I. Introduction

The idea of using static mode SIMS to study chemisorption was introduced by Benninghoven⁽¹⁾ many years ago. Thereafter quite a few pioneering experiments employing this technique were reported. Recently a few new experiments⁽²⁻⁴⁾ using a similar technique, but implemented by the use of a low energy primary ion beam were performed. A very interesting phenomenon was observed when we used this low energy static mode SIMS technique to study the chemisorption of oxygen on W(100)⁽³⁾ and Mo(100)⁽⁴⁾ single crystal surfaces. Amongst the various atomic and molecular ions, the following negative species: O^- , WO_2^- , and MoO_2^- showed features that reflected the different stages of chemisorption even in the submonolayer region. Such features included yield maxima, minima and abrupt changes in the rate of ion yield increase with oxygen coverage. With the help of ESD and AES to establish the oxygen coverage, these characteristics could be correlated with the formation of various periodic oxygen overlayer structures identified in LEED experiments. This discovery immediately suggested a new mode of using SIMS to study chemisorption. Apparently the low energy primary ions produced a lesser disturbance on the electronic state of the surface, allowing the escaping secondary ions to carry information on the chemisorption bond. In an attempt to elucidate the mechanism involved, a systematic study of the secondary ion

yields as a function of primary ion energy, ranging from 150 eV to 2 keV were made. Such data should be valuable in guiding the future use of this new technique.

II. Experimental Details

The experiment was performed inside an ion-pumped UHV system with a base pressure in the upper 10^{-11} range. High purity single crystal W(100) and Mo(100) samples were used. The samples with sizes of about .2"x.5" were polished mechanically and then electrolytically to roughly 4 mil thickness. The crystal orientation was better than 1° . The sample was resistively heated. Sample temperature was monitored with a W26%Re-W5%Re thermocouple. The sample cleaning procedure included heating the sample to 900°C in 10^{-6} torr O_2 for an hour to remove the carbon that segregated to the surface, followed by flash heating to 2000°C and 1400°C for W and Mo respectively to remove the oxide. The sample was then examined with AES to determine the surface cleanliness. The above procedure was repeated when necessary.

The primary ion beam used in this experiment was a Ne^+ beam collimated to a beam diameter of 4 mm, with a 3nA typical ion current. The angle between the beam and the sample was about 45° . When the gun was in operation, the Ne partial pressure was in the 10^{-7} torr range in the chamber. A liquid-nitrogen-cooled Ti sublimation pump kept the other residual gases, mostly hydrogen,

in the low 10^{-10} torr range. The oxygen partial pressure was usually in the 10^{-9} torr range during dosing and was controlled by a variable leak valve.

The secondary ions were detected using a quadrupole mass spectrometer with a counting channeltron. The sample surface was perpendicular to the mass spectrometer axis. The energy filter in front of the mass spectrometer blocked the line of sight of the mass filter and had an energy passband roughly from 0 eV to 30 eV.⁽⁵⁾ No attempt was made to energy analyze the secondary ions.

To determine the effect of different primary ion energies, it was important to compare the corresponding ion yields at the same oxygen coverages. To facilitate this procedure, special electronics were built to control the primary ion energy E_p , mass transmission M/e of the mass spectrometer and the polarity P of the ions to be detected. The switching circuit was synchronized with the counter such that it was possible to stay at one predetermined set of values $\{M/e, P, E_p\}$ for 10 seconds before changing to another set, with 10 seconds dead time in between to stabilize the electronics. With this arrangement, the yields of any two secondary ion species resulting from any combination of two E_p 's could be monitored every 40 seconds. In this experiment, the clean single crystal samples were exposed to oxygen with a partial pressure in the 10^{-9} torr range until a monolayer was accumulated in

1000 to 2000 seconds. In this way, two yield curves, plotted against time, were obtained simultaneously during each oxygen exposure. One particular ion yield, for example the O^+ yield from 2 keV Ne^+ sputtering [O^+ , 2 keV] was chosen as a reference for oxygen coverage. Then various secondary ion yields obtained in separate runs could be compared at equal oxygen coverages by monitoring the [O^+ , 2 keV] curve in every run or by cross correlation among such pairs of yield curves. This procedure made the exact knowledge of the oxygen dosage unnecessary as long as the oxygen coverage did not change by large amounts in 40 seconds.

Low energy static mode SIMS employing low primary ion densities ($<20 \text{ nA/cm}^2$) and low incident ion energies were expected to minimize the complication from radiation damage on the sample surface. We did not have LEED to monitor the crystal. In view of the very low current density used, reproducibility of the results and the many sharp features observed in the experiment, the surface damage was believed to be minor.

III. Experimental Results

A) O-W(100) System

The adsorption of oxygen atoms on W(100) at room temperature has been studied extensively using many surface analysis techniques.⁽⁶⁾ Molecular oxygen dissociates into atoms on W(100) surfaces. At low oxygen coverages, the atoms occupy fourfold sites randomly. At

about one third of a monolayer, the oxygen-oxygen interaction induces the formation of a p(4x1) periodic overlayer until the completion of a full monolayer. Then the oxygen atoms diffuse inward, forming a surface oxide.

i) O⁺

According to the current view of the sputtering process, oxygen atoms in the inner layers could contribute to the SIMS spectrum. In the experiment, the O⁺ yield was monitored at various Ne⁺ energies during the adsorption process. Figure 1 shows the results. Here the {O⁺, 2 keV} yield was used to represent the oxygen coverage. The ion yields were normalized to their maximum values for comparison. Initially, the ion yields were all proportional to each other at low oxygen coverages. Then they reached saturation at progressively higher oxygen coverages as higher energy Ne⁺ ions were used. In addition, we observed a small (~15%) decrease in the {O⁺, 150 eV} yield after reaching the maximum value. A separate experiment using AES showed that the O⁺ yield with 500 eV Ne⁺ was linear with oxygen coverage until close to monolayer completion. The data indicated that the O⁺ yields in general were roughly proportional to the oxygen coverages below a monolayer. Beyond a full monolayer, oxygen atoms in the inner layers could also contribute to the O⁺ yield although the probability of emission gradually decreased with lower Ne⁺ energy.

ESD and AES calibrations indicated that at 150 eV, the major contribution was from the first monolayer. The yield maximum was followed by a gradual decrease in the O^+ yield. This could be caused by slight changes in the ionization probability or the sputtering coefficient after oxygen diffused into the lower layers. The decrease was no longer appreciable with higher Ne^+ energies. Instead, contributions from the inner oxygen layers increased. This phenomenon was similar to the gradual decrease of sensitivity to inner atomic layers in AES. By using low energy primary ions, however, the characteristic depth could be made close to one lattice spacing in the case of SIMS.

ii) O^-

The O^- yield showed many interesting features. For experimental convenience, we chose the [O^+ , 500 eV] yield to represent the oxygen coverage. At least the first 75% of the O^+ yield came from the first monolayer, which is of primary interest in this experiment. Below one monolayer coverage, the O^- yield had two linear regions in the O^- vs O^+ plot as shown in Fig. 2. The low coverage, high slope linear segment was identified with the residing of oxygen atoms at random fourfold sites. On the formation of the $p(4 \times 1)$ overlayer structure at higher coverages, the curve bent over to a second linear segment with a smaller slope. Owing to the lack of space, we shall not elaborate on how we made

these structural identifications here, but refer the readers to reference 3. The ability to distinguish these two stages of chemisorption, as measured by the ratio of the two slopes, dropped from 4.4 at 150 eV(Ne^+) to 2.6 at 300 eV, 2.2 at 500 eV, 1.8 at 1 keV and 1.0 or no distinction at 2 keV. The O^- yield at coverages beyond a monolayer ($\text{O}^+/\text{O}^+(\text{SAT}) > 0.75$) also showed a more distinct transition at lower Ne^+ energies. After the completion of a monolayer, the O^- yield leveled off and even decreased slightly at 500 eV and below, but kept on increasing linearly at 1 and 2 keV.

B) O-Mo(100) System

The O-Mo(100) system is not as well understood as the O-W(100) system. This system was chosen, however, because it had shown a large number of oxygen overlayer structures when the adsorption temperature was 800°C.⁽⁷⁾ So this is a very useful system to demonstrate the ability of SIMS to distinguish chemisorption bonds and the effect of primary ion energies. Owing to the lack of space, we shall only discuss the O^- ion yield at 800°C in detail. The behavior of O^+ yield at 800°C was very similar to that shown in Fig. 1 for O-W(100). The [O^+ , 150 eV] yield saturated when the [O^+ , 500 eV] yield reached 90% of its maximum value. Again the [O^+ , 500 eV] yield was chosen to represent the oxygen coverage. Figure 4 shows the O^- yields plotted against the normalized [O^+ , 500 eV] yield. Even with 2 keV Ne^+ , very distinct features

were observed. After an initial rapid rise in signal, there was an abrupt change in slope at $O^+/O^+(SAT) \approx 0.45$ (first cusp). Then the yield decreased with increase in oxygen coverage until it reached a shallow minimum at $O^+/O^+(SAT) \approx 0.6$, followed by another slope change at $O^+/O^+(SAT) \approx 0.78$ (second cusp). After this coverage, the O^- yield decreased further until saturation. This is believed to be related to the formation of this sequence of oxygen overlayer structures: $c(2 \times 2)$, $p(1 \times 1)$, $\sqrt{5} \times \sqrt{5}$, $p(2 \times 2)$ and finally $p(1 \times 1)$ at saturation as observed by LEED.^(7,8) Similar features were observed with 1 keV and 500 eV Ne^+ . Below 500 eV, there was an increase in the O^- yield, especially at the first cusp. In fact, the yield at the first cusp was so much higher than that at the second cusp that the shallow minimum could no longer show up. The enhancement of O^- yield at the first cusp was most significant when 150 eV Ne^+ was used as shown by curve (a) in Fig. 3.

IV. Conclusions

Some of the limitations in the use of SIMS for chemisorption studies stem from our lack of understanding in the secondary ion formation mechanism. The present data should help us to get a better understanding of the physics involved. The emission of a secondary ion includes two physical processes. The first is the transfer of momentum to the surface atoms which causes sputtering. The second is the ionization process which involves an electronic

interaction between the escaping particle and the local electronic state of the emission site, which in turn is related to the chemisorption bond.

The behavior shown in Fig. 1 is believed to be mostly a consequence of the sputtering process. The geometric arrangement prevented atoms ejected by direct knock-ons to be detected by the mass spectrometer. Detected particles had to result from multiple collisions. Higher energy Ne^+ ions had a longer range in the target and a higher probability to eject an inner atom. At low Ne^+ energies, e.g. 150 eV, the probability of releasing an inner particle could be so low that the emitted particles were mostly surface atoms sputtered by the multiple surface collision mechanism.

The large variation of O^- yield with oxygen coverage as shown in Fig. 2 and Fig. 3 were probably not a consequence of sharp sputtering coefficient changes especially in view of the fact that the O^+ yield did not show similar features. Another peculiar behavior was that the O^- yield did not decrease appreciably with lower Ne^+ energy as O^+ , and other oxide ion yields did. In many cases, the O^- yield was even enhanced. All these observations could be a manifestation of changes in the ionization probability. The charge transfer involved in the bonding modified the local electronic configuration and hence the tunneling probability of an electron between the surface and the escaping particle. The

ionization probability should vary as the chemisorption bond changes during the different stages of adsorption.

In the ideal case if the incident Ne^+ ion only provides momentum for sputtering, it is conceivable that the initial bonding state of the surface atom is a factor determining its final charge state when sputtered. An important fact is the bond energy (~ 1 eV) is usually an appreciable fraction of the average escape energy, commonly a few eV. So the charged fraction of the sputtered particles should reflect any change in the chemisorption bond. Apparently, O^- which is less stable against neutralization than O^+ is more sensitive to such changes. Actually the incident particle not only transfers momentum, but also creates electronic excitations on the surface. Such excitations can perturb the initial electronic configuration and smear the bonding information. By using low energy primary ions, such perturbations should be reduced. This is consistent with our observation that the use of low energy Ne^+ ions enhanced the sensitivity to chemisorption bond changes.

Similar experiments were performed for WO_2^- and MoO_2^- . Higher primary ion energies just increased the ion yields without appreciably affecting the ability to distinguish different states of chemisorption. Apparently a favorable atomic arrangement on the surface could greatly enhance the yields of these ions.

Chemisorption bond changes were associated with rearrangements of the oxygen atoms, and hence would cause changes in the ion yields. More experimental data will be reported in the future.

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Figure Captions

Fig. 1. Normalized O^+ yields at various Ne^+ primary ion energies. The X-axis is the normalized $\{O^+, 2 \text{ keV}\}$ yield used as a representation for oxygen coverage.

Fig. 2. O^- yields at various Ne^+ primary ion energies. The X-axis is the normalized $\{O^+, 500 \text{ eV}\}$ yield used as a representation for oxygen coverage. The break in the slope is due to the formation of the $p(4 \times 1)$ oxygen overlayer on $W(100)$.

Fig. 3. O^- yield at 800°C at various Ne^+ energies. The X-axis is the normalized $\{O^+, 500 \text{ eV}\}$ yield used as a representation for oxygen coverage on $Mo(100)$.

FIG 3