## Surface Extended-X-Ray-Absorption Fine Structure by Means of Photon-Stimulated Ion Desorption: O on Mo(100)

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The photon-stimulated desorption (PSD) of  $O^+$  ions from the  $\alpha$ -oxygen phase on Mo(100) has been monitored through and above the Mo  $L_1(2s)$  absorption edge (2866 eV) and is compared to the absorption spectrum of clean Mo(100). The PSD ion yield is shown to reveal the extended-x-ray-absorption fine structure of Mo surface atoms which were bonded to oxygen atoms prior to their desorption. Studies of the present kind provide a new powerful tool for surface structure investigations.

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Photon-stimulated desorption (PSD) of ions from surfaces has recently been shown by Knotek, Jones, and Rehn<sup>1</sup> to be coupled to the core-electron excitation process. For adsorbates on surfaces a core hole on an adsorbate or a surface substrate atom is filled by an intra-atomic or interatomic Auger transition which results in holes in the valence band breaking the bond of the adsorbate complex.<sup>2</sup> Since all processes which are linked to filling a core hole which is created by photon absorption provide a measure for the respective absorption coefficient, it has been suggested<sup>1, 3, 4</sup> that the PSD ion yield should be usable as a signal for surface extended-x-ray-absorption fine-structure (SEXAFS) measurements.<sup>5, 6</sup> Here, we report the first study of this kind.

The purpose of the present paper is to establish PSD as a new powerful detection technique for SEXAFS and, therefore, surface structure measurements. This is accomplished by studying the  $\alpha$ -oxygen phase on Mo(100) as an example.<sup>4, 7-11</sup> We show that the PSD O<sup>+</sup> yield indeed accurately follows the absorption coefficient of Mo surface atoms out to several hundred electronvolts above the Mo  $L_1$  absorption edge. The PSD active adsorbate complexes are found to consist of oxygen atoms bonded to the Mo(100) surface without local

rearrangement of the Mo surface atoms. This is surprising in view of the large previously reported oxidelike Mo 3p chemical shift of 2.9 eV<sup>4</sup> which would indicate local oxide structure formation.

Experiments were carried out on the new ultrahigh vacuum compatible double-crystal monochromator JUMBO<sup>12</sup> at the Stanford Synchrotron Radiation Laboratory (SSRL). With Ge(111) crystals installed this monochromator covers the range 2000-4200 eV. The storage ring SPEAR operated at 3.2 GeV and ~80 mA maximum current in a two- or three-bunch mode (period 390 or 260 nsec). The ion flight times from the sample to the channelplate detector<sup>4</sup> were measured relative to the "prompt" photon pulses of SPEAR of known periodicity and allowed a mass resolution of  $M/\Delta M = 16$  at mass 16.<sup>4</sup> The ion and electron yield<sup>13</sup> signals from the sample were flux normalized with use of the electron yield signal from a Cu grid positioned in the beam.<sup>13</sup> The Mo(100) single crystal was cleaned by using established procedures.<sup>4</sup> Experiments were carried out at room temperature at a base pressure of  $< 3 \times 10^{-10}$  Torr.

Figure 1 compares the total electron yield Mo-L<sub>1</sub> EXAFS for a clean Mo(100) sample with the  $O^+$ 



FIG. 1. Comparison of (a) the total electron yield EXAFS for a clean Mo(100) sample and (b) the PSD O<sup>+</sup> yield for 100 L O<sub>2</sub> on Mo(100) ( $\alpha$ -oxygen phase), above the Mo  $L_1$  edge. The structures at 2840 and 3290 eV are Bragg "glitches" as discussed in the text.

yield signal obtained from a Mo(100) surface exposed to 100 L [l langmuir (L) =  $10^{-6}$  Torr sec] oxygen.<sup>14</sup> In both cases the x-ray beam was incident on the sample at a grazing angle of  $\sim 20^{\circ}$ . Both spectra show a sharp rise in count rate at the Mo  $L_1$  absorption edge around 2870 eV and EXAFS oscillations are clearly visible up to 700 eV above the edge. The oscillations above threshold are closely the same in frequency with an overall reduction in amplitude for the  $O^+$  yield spectrum. The threshold structures are different with a pronounced spike on the edge for the ion yield spectrum. The structures around 2840 and 3290 eV are caused by Bragg reflection of the Mo(100) single crystal and multiple Bragg reflection in the Ge(111) monochromator crystals, respectively. Both structures can be removed as indicated by the dashed lines in Fig. 1. In the following we shall compare the EXAFS oscillations in the 3000-3600 eV range.

The EXAFS oscillations  $\chi(k)k^3$  obtained from Fig. 1 after background subtraction<sup>15</sup> and normalization to the  $L_1$  edge jump are shown in Fig. 2. Within statistics<sup>14</sup> the two signals are identical in frequency with a reduction in amplitude by a factor of 2 for the O<sup>+</sup> yield spectrum. The Fourier transforms of the two signals for the EXAFS range 7.8–13.0 Å<sup>-1</sup> are shown in Fig. 3. Both transforms are dominated by a single peak A. Detailed analysis following previously discussed procedures<sup>15</sup> shows that the peaks in Fig. 3 fall



FIG. 2. EXAFS oscillations above the Mo  $L_1$  edge as a function of photoelectron wave vector. (a) Electron yield from clean Mo(100). (b) O<sup>+</sup> yield from  $\alpha$  oxygen on Mo(100). The oscillations are almost identical in frequency but note the difference in amplitude.



FIG. 3. Absolute values of the Fourier transform of the EXAFS signals in Fig. 2 for the range 7.8 Å<sup>-1</sup>  $\leq k$   $\leq 13.0$  Å<sup>-1</sup>. Note that peak *A* is twice as large for the electron yield EXAFS case indicating twice as many nearest neighbors as discussed in the text.

within 0.03 Å of each other. The electron yield EXAFS amplitude corresponding to peak A is bigger by almost exactly a factor of 2 (± 10%). From the total electron yield EXAFS spectrum it is clear that peak A in Fig. 3 corresponds to the Mo-Mo nearest-neighbor distance R = 2.73 Å in bcc Mo metal.<sup>16</sup> Because the electron yield signal originates from atoms within 50–100 Å of the (100) surface the corresponding EXAFS spectrum is representative of *bulk* Mo atoms with only a small (< 10%) surface contribution.

The ion yield  $\gamma_{ion}$  following the excitation of a photoelectron from a core level *n* is proportional to the partial absorption coefficient  $\mu_n(h\nu)$  of this level according to<sup>4</sup>

$$\gamma_{\rm ion}(h\nu) \sim (1-f) P_n \mu_n(h\nu). \tag{1}$$

Here  $P_n$  is the probability for Auger transitions into the core hole in shell n which result in holes in the valence region such that the surface complex is transformed into a repulsive ionic state.  $P_n$  is independent of  $h\nu$  but depends on the overlap of the valence and core wave functions involved. f is the probability for reneutralization of the repelled ion causing either the recapture of the ion or its desorption as a neutral. The survival probability (1-f) is also  $h\nu$  independent but depends strongly on the overlap of valence wave functions of the repelled ion and its neighbors which leads to the high site specificity discussed previously.<sup>1,4,17</sup> Because of the vanishing 1 - fterm for bulk atoms the PSD signal originates exclusively from surface atoms. Above the Mo  $L_1$  edge the O<sup>+</sup> desorption follows an *inter*atomic Auger transition of an O valence electron into the 2s core hole of a Mo neighbor at the surface. The O<sup>+</sup> yield is thus a measure of the absorption coefficient of those Mo surface atoms which were bonded to oxygen atoms prior to their desorption as  $O^+$ . The  $O^+$  yield EXAFS should reveal the Mo-O and Mo-Mo nearest-neighbor distances within the surface complex without superposition of the bulk Mo-Mo distance.

Peak A for the O<sup>+</sup> yield spectrum is assigned to the Mo-Mo distance of a *surface* Mo atom with its nearest Mo neighbors in the second layer. This assignment is made on the basis that (i) peak A falls almost exactly at the same distance as for the bulk electron yield spectrum, (ii) the EXAFS amplitude corresponding to peak A shows the same shape as a function of k for both cases (maximum at ~10 Å<sup>-1</sup>),<sup>18</sup> and (iii) the overall amplitude of the ion yield EXAFS is reduced by almost exactly (within 10%) a factor of 2. This latter factor arises from the fact that a Mo atom on the Mo(100) *surface* has only four nearest Mo neighbors as compared to eight neighbors in the bulk. Note that because of cubic symmetry the EXAFS is independent of polarization.<sup>15</sup> The fact that the EXAFS amplitude is reduced by a factor of 2 for the ion yield can be regarded as direct proof for the Auger-induced desorption mechanism. If desorption was simply a consequence of valence excitations caused by secondary electrons both spectra should exhibit *equal* amplitudes.

The guestion arises if the shorter Mo-O distance  $(\sim 2.0 \text{ Å})$  at the surface can be determined in addition to the Mo-Mo distance (2.725 Å). The Mo-O EXAFS will be sizable only at low k values because of the rapidly decreasing size of the O backscattering amplitude.<sup>18</sup> There are indeed changes on the low-distance side of peak A if the low-k EXAFS region 5-8 Å<sup>-1</sup> is included in the analysis. However, our present data do not allow a reliable determination of the shorter O-Mo distance because the low-k EXAFS region above the  $L_1$  edge contains a nonnegligible contribution from the EXAFS above the  $L_3$  and  $L_2$  edges which lie 346 and 241 eV below the  $L_1$  edge, respectively. The  $L_{3,2}$  EXAFS does not contribute in the high-*k* region 8-13 Å<sup>-1</sup> used for derivation of the Mo-Mo distance in Fig. 3 because of a negligible amplitude and an increasingly different (lower) frequency with increasing k.<sup>19</sup>

The fact that the EXAFS for Mo atoms in bulk Mo and at the  $\alpha$  oxygen on Mo(100) surface are essentially identical shows that the  $\alpha$ -oxygen phase forms without reconstruction of the Mo(100)surface. This excludes any local oxide structure formation as might be expected from the large oxidelike Mo 3p chemical shift (2.9 eV) for the oxygen-coordinated Mo surface atoms.<sup>4</sup> This points to a very similar chemisorption structure as for the high-oxygen-coverage phase on W(100)discussed by Madey<sup>20</sup> where the O atoms are believed to be bonded to one W surface atom of the outmost substrate layer. The high desorption rate and large chemical shift for the high-coverage (minority)  $\alpha$ -oxygen phase on Mo(100) can be explained by a highly *ionic* chemisorption bond as opposed to a more *covalent* like O-Mo bond for the low-coverage (majority) phase where oxygen is believed to occupy the fourfold hollow site.

The present measurements establish PSD as a new powerful detection technique for SEXAFS studies. In many cases such studies can offer unique advantages over all other known methods VOLUME 45, NUMBER 23

of surface structure determination. It is now possible to obtain structural information of specific chemisorption sites which are present in addition to other (e.g., majority) sites with smaller desorption cross sections. It is also possible to distinguish between sites where a given adsorbate (e.g., O) is present in atomic or molecular form (e.g., by  $O^+$  vs  $OH^+$  or  $O_2^+$  detection). PSD SEXAFS measurements can be carried out above both the substrate as well as the  $adsorbate^4$  absorption edges and offer thus additional information as compared to electron yield SEXAFS (adsorbate edge only) studies.<sup>5,6</sup> Finally, by measuring H<sup>+</sup> desorption structural studies of the interaction of hydrogen with surfaces can be performed, even if the surface is disordered.

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