Study of the Oxidation of W(110) by Full-Solid-Angle Photoelectron Diffraction with Chemical State and Time Resolution

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INTRODUCTION

The brightness of third-generation synchrotron radiation from beamline 9.3.2 at the Advanced Light Source [1(a)] has been combined with the high-intensities and energy resolutions possible with its advanced photoelectron spectrometer/diffractometer experimental station [1(b)] in order to study the time dependence of the oxidation of the W(110) surface. This has been done via chemical-state-resolved core-level photoelectron spectroscopy and diffraction. This system has been studied previously by other methods such as LEED and STM [3-6], but several questions remain as to the basic kinetics of oxidation and the precise adsorption structures involved. By studying the decay and growth with time of various peaks in the W $4f_{7/2}$ photoelectron spectra, it should be possible to draw quantitative conclusions concerning the reaction kinetics involved. We have also measured full-solid-angle photoelectron diffraction patterns for the two oxygen-induced W states, and these should permit fully defining the different structures involved in this oxidation process.

RESULTS AND DISCUSSION

The surface of a clean W(110) surface at room temperature was reacted with oxygen at a pressure $3x10^{-9}$ Torr O_2; the base pressure in the chamber before beginning to leak in oxygen was $1.3x10^{-10}$ Torr. The W $4f_{7/2}$ spectrum taken for the clean W(110) surface at the onset of oxidation is shown in Fig. 1(a). This figure shows two well-resolved peaks, with a 320meV binding energy shift between them and the peak at higher kinetic energy (lower binding energy) being attributed to the top layer of tungsten atoms with no overlying adsorbate [2]. Spectra such as this were taken every 20 sec over a period of 70 min. Figs. 1(b) and (c) show later spectra taken at 35 min and 70 min. By 35 min., the surface peak is gone, indicating that the top layer of tungsten is completely covered by some first adsorption state(s) of hydrogen [2] and/or oxygen. There are two chemically shifted peaks, one at a higher binding energy with +350 meV shift relative to bulk that we assign to a first and more weakly bound chemisorbed species, and the other with a +730 meV that we assign to a second and more strongly bound "incipient-oxide-like" species. The 730 meV peak is found to persist up to a 1 monolayer (ML) oxygen coverage where, with oxidation at higher temperature and pressure, it forms a highly ordered (1x1)-(1x12) long-range structure as seen in both scanning tunneling microscopy (STM) [6] and low energy electron diffraction (LEED) [7]. Figs. 1(b) and (c) make it clear that the 350 meV state grows in first, but that the 730 meV state becomes dominant by the end of the time interval. Fitting peak shapes to this set of spectra now permits determining the quantitative time dependence of all four of the peak intensities observed, as shown in Fig. 1(d). From this figure, we can see that the decay of the surface peak occurs over the first 10-15 min., that it is accompanied by a growth of the bulk peak,

and that it is only after the 350 meV peak reaches a maximum at about 20-25 min. that the 730 meV peak begins to grow in, at the expense of the 350 meV peak. These results clearly suggest a linkage in the kinetics of these adsorption and oxidation processes. We are presently analyzing these first-of-a-kind data in order to derive a more precise kinetic model.

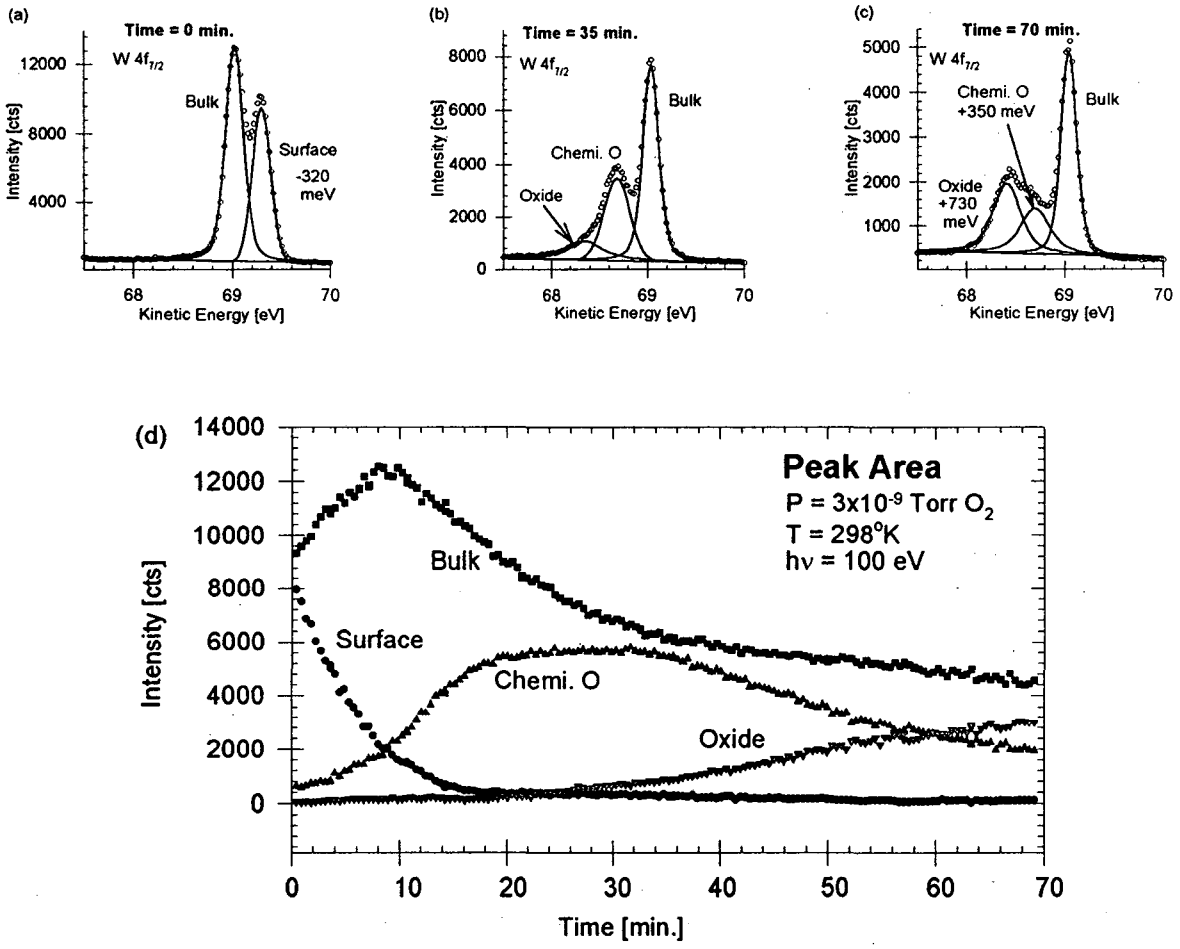

Figure. 1. Time and state resolved W $4f_{7/2}$ photoelectron spectra for a clean W(110) surface exposed to oxygen: (a) t = 0 min.--Initial clean surface showing the surface core level shifted peak at -320 meV with respect to bulk; (b) t = 35 min.--Surface after 35 min. exposure showing the two oxygen-induced peaks at +350 meV and +730 meV; (c) t = 70 min.--Final spectrum of the series after 70 min., showing the increase of the oxide peak at the expense of the chemisorbed oxide peak; (d) The time dependence of the four peaks observed in these spectra.

We have also measured full-solid-angle photoelectron diffraction patterns for both the chemisorbed and oxide peaks in the W $4f_{7/2}$ spectrum, with these then permitting a direct structural determination for the two W states involved. The structure of the oxide state at 730 meV has not been determined before, beyond the indication of a threefold adsorption site from STM [6(a)], although LEED has been used to determine the structure of what is probably the 350 meV state [6(b)]. The LEED pattern shows superstructure spots whose symmetry depends on the oxygen coverage and the heat treatment during and after adsorption [this work and 6(b)]. For our study, one monolayer of oxygen is deposited, so that, by the end of the exposure, the LEED exhibits a (1x1)-(1x12) pattern. We here discuss the results for the oxide peak at 730 meV associated with this (1x12) structure, with analysis for the other peak at 350 meV currently in progress. This oxide was formed in a purer state by doing a separate surface reaction at a pressure of $1.3x10^{-6}$ Torr of oxygen and a temperature of 700°C, a recipe used in a prior STM

study [6] and leading to a sharp (1x1)-(1x12) LEED pattern [7]. For this case, only a single oxide peak at 730 meV was observed, together with the bulk peak. The angle between the linearly-polarized incident radiation and the electron emission direction was fixed at 70°, with the sample being rotated on two perpendicular axes to obtain the full diffraction pattern. The excitation energies used were 127 eV and 170 eV, via third- and fourth- order light from the spherical grating monochromator on beamline 9.3.2 [1(a)]. We have measured ~900 W $4f_{7/2}$ spectra over nearly the full solid angle above the surface, spanning the takeoff angle range from θ = 9° to 90° (=normal emission) in 3° steps and the 180° azimuthal angle range from W [1-10] to [-110]. Fitting these spectra with appropriate peak shapes then permitted deriving separate diffraction patterns from each peak. The variation of radiation flux with time was normalized out in determining the final intensities. The experimental diffraction pattern for the oxide peak with 170 eV excitation is shown in Fig. 2(a).

The data in Fig. 2(a) have been analyzed by comparing experiment to theory via R-factors, with corollary structural information coming as well from a similar analysis of an experimental diffraction pattern obtained with higher-energy x-ray excitation at 1,487 eV [7]. The final optimum structure is for the oxygen in this incipient oxide structure to sit in a quasi-threefold hollow site on the W(110) surface, with an interlayer separation from the first W layer of 0.95 ± 0.05 Å and a W-O bond distance of 1.79 Å that is very close to that found in bulk W oxides. The final theoretical diffraction pattern for the best fit geometry is shown in Fig. 2(b), and it is in excellent agreement with experiment. Analysis of the data obtained with 127 eV excitation leads to a similar structural conclusion.

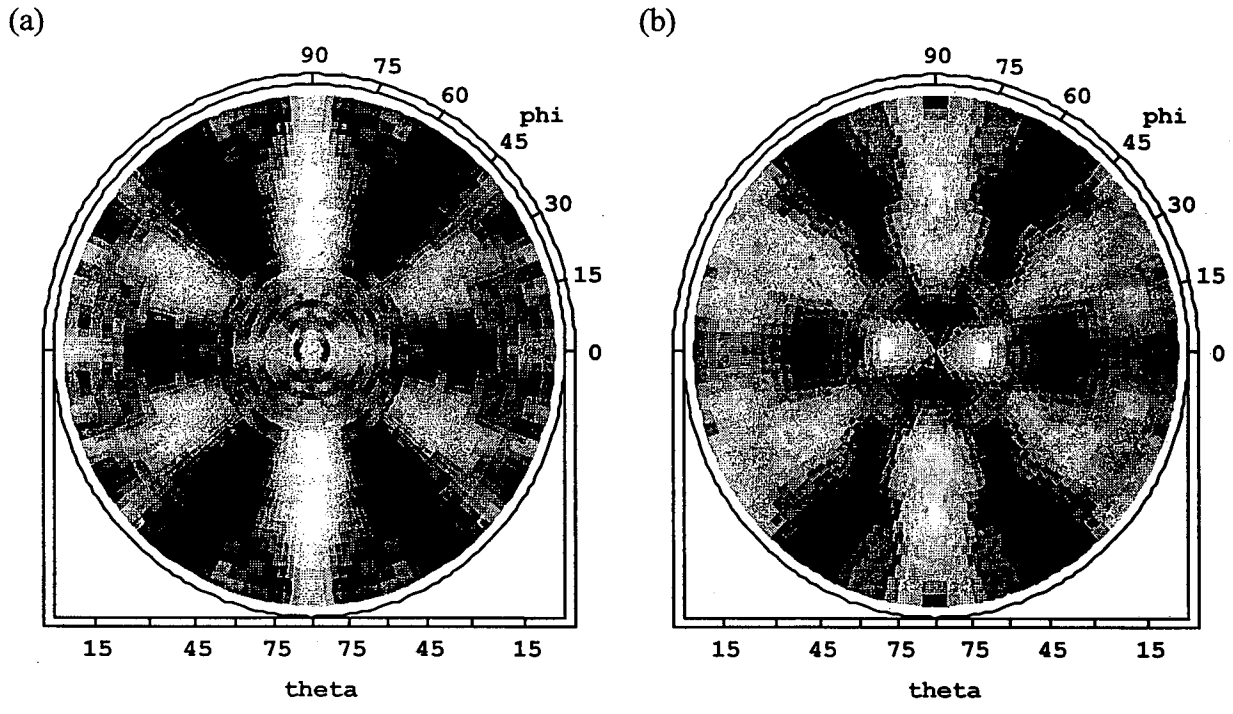

Figure 2. Full-solid angle diffraction from the top layer of atoms of O/W(110) (1x1)-(1x12); (a) experimental data; (b) multiple scattering theory with oxygen atoms occupying the threefold hollow sites at a bond distance of 1.79 Å, and an interlayer distance of 0.95 Å.

CONCLUSIONS

This study thus demonstrates the considerable potential of time and chemical-state resolved photoelectron spectroscopy at a third-generation synchrotron radiation source for studying surface reaction kinetics, as illustrated for the four-state system involved in the oxidation of clean W(110). Being able to simultaneously use photoelectron diffraction to determine the local atomic geometries around species with different chemical states, as illustrated here for the incipient oxide state in the O/W(110) system, represents another unique capability that should be broadly applicable to various surface reactions and epitaxial growth processes.

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