OXIDATION OF Mo(001) SURFACES

I. K. ROBINSON
Department of Physics
University of Illinois
Urbana, IL 61801, USA

ABSTRACT. X-ray diffraction using synchrotron radiation is now sufficiently sensitive to investigate surface structure in a fairly routine way. Among its advantages is the straightforward kinematic interpretation of the atomic arrangement at the level of 0.01Å, where chemically relevant details of bonding become apparent. The oxygen-induced reconstruction of Mo(001) has recently been studied and sheds light on the mechanism of oxidation.

1. Introduction

A major attraction of the use of photon-based techniques in studies of the electrochemical interface is that photons (optical or hard X-rays) can traverse a macroscopic quantity of liquid *en route* to the interface. Most other available experimental techniques with surface sensitivity attain that sensitivity by using a non-penetrating probe, electrons for example. These cannot penetrate the liquid of the ideal sample geometry, and require tricks to be used, such as emersion, with all the accompanying caveats.

Photon-based methods are fundamentally different. They use the special *symmetry* of the interface for their specificity. Second-harmonic and sum-frequency generation, for example, use the non-inversion symmetry of the third-order dielectric susceptibility to obtain a unique signal from the interface. Surface X-ray diffraction similarly uses the broken translational symmetry of the interface for the same purpose. The diffraction from a 3D crystal is confined to sharp spots, while that of a truly amorphous or liquid ('0D') material is diffused everywhere. A flat interface between a crystal and a liquid has diffraction that has special properties: it is diffuse in the direction perpendicular to the interface, but sharp in the direction parallel to the interface. This makes possible the measurement of the integrated intensity distribution, needed for quantitative structural analysis. This is both straightforward and accurate, even though much greater quantities of crystal and liquid are present at the same time: the isotropically diffuse signal is subtracted as background, while the sharp 3D Bragg peaks can be avoided altogether.

Surface X-ray diffraction is however limited by the same constraints that gives its advantage. In order to establish clearly identifiable diffraction it is necessary for the electrode to be a single crystal and for the electrolyte to be an ideal liquid with a uniform scattering function. Moreover, for the diffraction pattern to be interpreted with certainty, it must be close to ideally 2D and unambiguously distinguishable from 0D and 3D. This limits us to interfaces that are at most a few atomic layers thick. Some problems of interest in electrochemistry are not so readily idealised. Corrosion of polycrystalline or composite materials with

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complex grain structures would not be easily undertaken. Similarly, not much information could be obtained about thick passivation layers that do not have specific ordered atomic structures.

Before the advent of scanning tunnelling microscopy (STM) and surface X-ray diffraction, few techniques were available to examine the electrochemical interface at the atomic level. It is already apparent that a variety of ordered structures has been found to exist under controlled, reversible preparation conditions. Unlike in the field of surface science where most of the structures were known before the X-ray techniques were developed, the existence of structures at the electrochemical interface is largely unexplored, notably by the present author. For these reasons this paper is about a surface structure in vacuum and not about an electrochemical system. It should serve as a tutorial for the kind of results to be expected from electrochemical interfaces (subject to the restrictions outlined about) that should be uncovered in the next few years.

2. Oxygen on Mo(001)

The wide range of oxides known for Mo demonstrate a dramatic variation of coordination and valency in their bulk crystal structures [1]. Given that much less is known about the surface oxides, a good place to start is the Mo(001)/O adsorbate system. This is an ideal model for understanding the role of precursors in the oxidation of Mo. Despite the fact that there have been a number of thorough LEED studies [2-10] over the years, not much more than the symmetry is known of the actual structure of these phases. The sequence of symmetries observed is completely different at different temperatures: room temperature (RT) adsorption of O on Mo(001) gives a consecutive series of ordered structures, c(2×2), followed by 6×2, then 6×1, then 3×1 and finally 1×1 [6,8,9]. On the other hand, high temperature reaction with O (above 1000K) gives the series, c(4×4), 2×1, $\sqrt{5}\times\sqrt{5}$, 2×1, c(2×2), and eventually produces facetted structures [2-10]. The formation of these facetted states has been investigated and found to result in oxide layers [5,7,10] that start at 1000L (1 Langmuir = 10^{-6} Torr sec) and saturate at 5000L [10]. Thermal desorption from the oxide state yields the high temperature series of surface structures in reverse order [6-10]. The likely reason for the variation with temperature is that the Mo atoms are mobile at 1000K so can form structures that involve diffusion in which the stoichiometry can change. At room temperature the number of Mo atoms in the structure must be conserved; most probably the RT structures are arrays of adsorbed O atoms with packing density corresponding to the coverage. For this reason it is the high temperature structures that are more interesting from the point of view of studying oxidation.

The oxygen coverages corresponding to each state have been determined by careful quantitative Auger spectroscopy measurements [8-10]. Of the various high-temperature phases, the $\sqrt{5}\times\sqrt{5}$, which occurs at an O coverage of 0.8 monolayers (ML), appears to have the widest stability range. It is also the highest coverage chemisorbed phase that is well-ordered, in the sense of having a sharp LEED pattern. All structures with higher coverages are somewhat diffuse in LEED, a fact that has been attributed to the onset of O-induced facetting [5-10] of the surface, followed by three dimensional oxidation. Our x-ray diffraction