Investigation of underlayer formation by oxygen on Al(111) and Ti(0001)

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High-resolution electron energy loss spectroscopy is used to investigate the initial stage of oxide formation on Al(111) and Ti(0001) surfaces. Analysis of the O/Al(111) vibrational data based on lattice dynamical slab calculations confirms underlayer formation as a precursor to oxidation. These results help account for some of the novel properties associated with oxygen chemisorption on Al(111) and Ti(0001) surfaces and also illustrate the ability of vibrational spectroscopy to provide surface structure information which complements results of other structure sensitive techniques.

I. INTRODUCTION

The oxidation of Al(111) and Ti(0001) surfaces appears to be preceded by a precursor chemisorbed state which is more complex than a simple chemisorbed species on the surface. The initial chemisorption of oxygen and subsequent chemisorbed stages which precede oxide formation on Al(111) have been studied by numerous experimental methods,[1-14] and by first principles calculations[15-18] which yield energy bands, work functions, oxygen binding energies, and other relevant parameters. High-resolution electron energy loss spectroscopy (EELS) studies of the O/Al(111) system[12] were able to demonstrate clearly and unambiguously that underlayer formation accompanied surface chemisorption. Lattice dynamical calculations[13,14] provided an appropriate model for the overlayer/underlayer configuration which, with the EELS data, formed the basis for computational studies. These computational studies, along with the EELS and other experimental work, have now established a fairly clear picture of the surface and subsurface binding sites, as well as reasonable explanations for many of the inconsistent results obtained in early studies of the O/Al(111) system.[19]

The initial chemisorption of oxygen (or nitrogen) on Ti(0001) exhibits properties which are similar to those observed on Al(111).[20-26] Studies of the O/Ti(0001) system[22-26] suggest that two chemisorbed states of oxygen exist on Ti(0001): a tightly bound α state at low coverages characterized by a well-ordered $p(2\times 2)$ LEED pattern and work function below that of the clean surface, and a β state characterized by a (1×1) LEED pattern and a work function higher than the clean surface value. Heating was observed to convert the β state to the α state. Such behavior is similar to what has been observed for overlayer to underlayer conversion in the O/Al(111) system.

In this paper we discuss the use of high-resolution electron energy loss spectroscopy to study underlayer formation associated with oxygen chemisorption on Al(111) and Ti(0001) surfaces. We show that surface vibrational spectroscopy is sensitive to underlayer formation on these surfaces and that it provides information which is not directly available from other surface probes.

II. EXPERIMENT

Our experiments were carried out in a spectrometer which incorporates EELS optics (a modified Leybold–Heraeus ELS-22),[27] LEED optics, Auger optics, and a quadrupole mass spectrometer. Sample preparation techniques for our investigation of O/Al(111) have been discussed in previous publications[12,13] which also describe, in more detail, the experimental apparatus, experimental techniques, and the lattice dynamical techniques[13,14] used to calculate vibrational spectra based on slab models of the adsorbate systems. The titanium crystals were spark cut from a 3/8 in. diam rod[28] after determining the (0001) direction within ± 1 by x-ray Laue techniques. After mechanical polishing with alumina powder down to 1 μ grit, the samples were cleaned *in situ* by sputtering with 2 keV argon ions at pressures of 5×10^{-5} Torr while heating to 900 K. Auger spectroscopy and LEED were used to characterize the sample surfaces and to determine the oxygen concentration and surface periodicity after exposure, which was accomplished by admitting high purity gas at pressures ranging from 10^{-9} to 10^{-5} Torr. Gas doses were determined using a nude ionization gauge, and sample temperatures were measured by a Chromel–Alumnel [for Al(111)] or tungsten–rhenium thermocouple clamped or spot welded to the edge of the crystal.

III. THE O/Al(111) SYSTEM

Chemisorption properties of oxygen on aluminum surfaces have been extensively studied both theoretically and experimentally, and a review article[19] on the O/Al system has recently been published. Most of our EELS work on the O/Al(111) system is described in the literature,[12-14] but we have carried out some additional lattice dynamical modeling studies which were suggested by recent self-consistent calculations.[17,18] This section reviews our previous conclusions for O/Al(111) and discusses the new results of our most recent surface lattice dynamical study. A preliminary account of corresponding studies of oxygen chemisorption on Ti(0001) is presented in the following section.

Early experimental efforts to characterize the initial stage of oxidation of Al(111) surfaces resulted in a number of conflicting conclusions.[29] Several distinct phases of chemisorbed oxygen were reported including a molecular phase,[10] as well as pressure dependencies in the formation of the various phases. Low energy electron diffraction studies[2-4] placed the oxygen atom at various heights above the threefold hollow sight (1.46, 1.33, and 1.54 Å) and other LEED results[1] suggested that the (1×1) pattern for O/Al(111) cor-

responded to an underlayer 0.73 Å below the surface and an overlayer 0.80 Å above the surface. Work function measurements[5–9] also yielded inconsistent results, but most of these studies were consistent with a small decrease in work function ($\Delta\phi < 200$ meV) for an oxygen dose of less than 50 L (1 L = 10^{-6} Torr s). These conflicting experimental results served as the motivation for our EELS studies of the O/Al(111) system.

Some of our previous published EELS spectra for O/Al(111)[12] are reproduced in Fig. 1 for reference purposes. In nearly all of the spectra there are three peaks at 40–50, 80, and 105 meV. The 80(105) meV peak was experimentally assigned to the vibration of overlayer (underlayer) oxygen atoms perpendicular to the surface on the basis of the variation of loss peak intensity after sputtering or annealing. No peaks were observed in off-specular geometry which were not observed in specular geometry. At the time of these experiments, the upper limit on electron kinetic energy for our spectrometer was 22 eV. With our modifications to the electron optics,[27] we can now achieve kinetic energies at the target of 300 eV. Higher kinetic energies should allow the observation of the oxygen modes parallel to the surface in off-specular geometry. Since both the overlayer and underlayer oxygen are present simultaneously in varying proportions, and this proportion can change with time at room temperature due to diffusion of overlayer oxygen beneath the surface, many of the earlier conflicting results on this system can be attributed to differences in the properties of overlayer and underlayer oxygen.

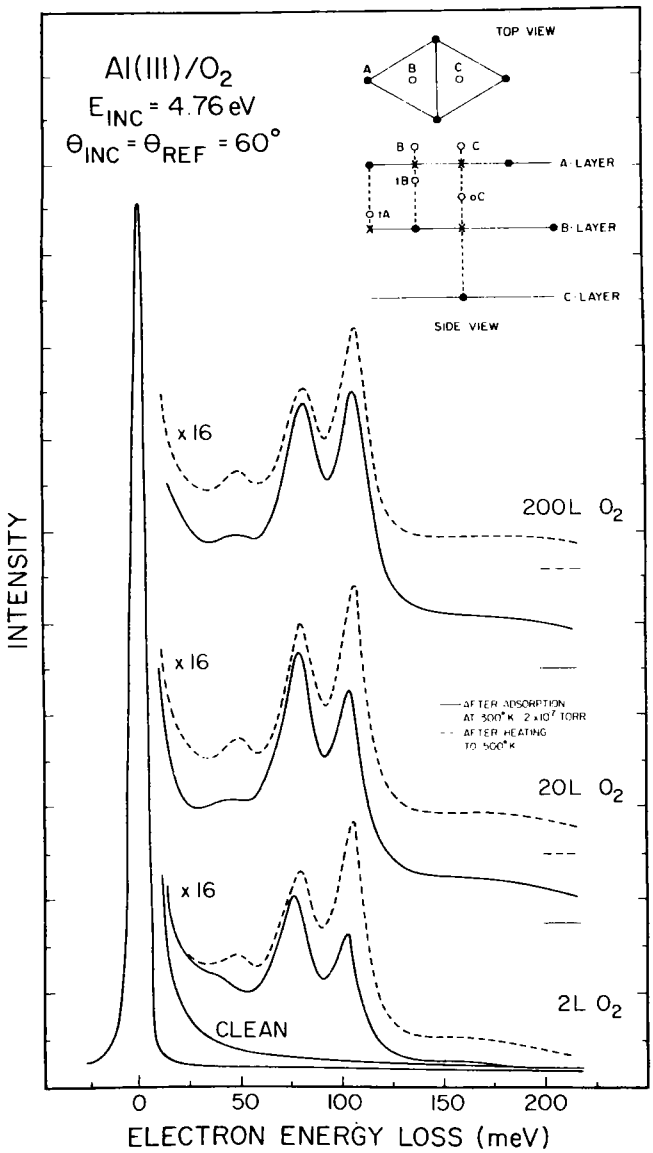

FIG. 1. EELS spectra before and after annealing for 2, 20, and 200 L (1 L = 1×10^{-6} Torr s) doses of oxygen on Al(111); insert, lattice model for the Al(111) surface illustrating several high-symmetry locations where oxygen atoms could reside.

These peak assignments were confirmed by lattice dynamical calculations[13,14] which assumed no reconstruction of Al atoms and no alteration in Al–Al force constants from the bulk value. Only three nearest neighbor force constants involving oxygen atoms were included: overlayer oxygen to surface aluminum (assumed equal) and overlayer oxygen to underlayer oxygen. The intralayer oxygen–oxygen force constants were assumed to be zero, but they have no effect on the vibrational mode energies at $\bar{\Gamma}$, so they did not affect the fitting of the calculated dipole-allowed mode energies to the experimental peak energies. With these assumptions, we concluded that the overlayer oxygen occupies the threefold hollow (*c*) site above the third layer Al atoms, and the underlayer oxygen occupies the tetrahedral (*tB*) site above the second layer Al atoms (refer to insert of Fig. 1). This is the configuration proposed by Norman *et al.*[11] on the basis of SEXAFS experiments.

Bylander and Kleinman[18] have recently calculated the binding energy of a double layer of oxygen on Al(111) and found the minimum energy occurred with a configuration involving adsorption of underlayer oxygen in a modified octahedral site, relaxation of the Al surface, and placement of the underlayer oxygen closer to the second Al layer than the first (rather than halfway in between). Based on this result, the lattice dynamical calculations were repeated for the reconstructed C/*mo*C configuration with the underlayer oxygen in a modified octahedral C site. In addition, the force

TABLE I. Nearest-neighbor central force constants obtained by fitting the modes polarized perpendicular to the surface to 105, 80, and 44.5 meV, assuming oxygen adsorbed above the surface 0.61 Å, the surface aluminum layer relaxed inward 0.0586 Å, and the underlayer oxygen 0.91 Å above the second layer of aluminum (Ref. 18). Both the overlayer and underlayer oxygen atoms are above third layer aluminum atoms (C sites).

Nearest neighbor central force constants (N/m)		
Bulk aluminum:	21.0	21.0
Al(1)–Al(2):	5.0	4.9
O(1)–Al(1):	560.0	458.0
O(2)–Al(1):	32.0	140.9
O(2)–Al(2):	410.0	176.1
O(1)–O(2):	160.0	211.4
Surface mode polarizations and energies (meV)		
Parallel	139.0	127.6
Perpendicular	104.9	104.9
Parallel	112.2	82.7
Perpendicular	80.2	80.0
Perpendicular	44.6	44.6
Parallel	20.7	35.0

constant between the first and second layer of Al was allowed to vary from the bulk value, and the force constants between the underlayer oxygen and the first and second layer Al were allowed to be different. There are now five force constants to vary (listed in Table I) along with the bulk Al force constant. Two sets of force constants were obtained which fit the EELS spectra, one of which seemed fairly reasonable on the basis of Bylander and Kleinman's calculated electronic densities.[17] With five parameters and three data points to fit, there is probably a continuum of force constant values which would fit the present data. Therefore, it is possible for the C/*tB* and C/*mo*C configurations to both be consistent with the available vibrational spectra, although quite different assumptions are made and different force constants obtained in the two models. Additional data on the oxygen modes parallel to the surface would almost certainly resolve the question of the correct underlayer site, as well as pinning down the correct force constants.

IV. THE O/Ti(0001) SYSTEM

The oxidation of the (0001) face of single crystal hexagonal-close-packed Ti has been investigated with AES and energy loss spectroscopy,[23] with UPS and electron and photon stimulated desorption,[24] and with appearance potential spectroscopy, AES, LEED, and work function measurements.[22] The consensus is that there is an initial "chemisorbed" α phase, possibly below the Ti surface, and a second "oxide" β phase beginning somewhere between 3 and 10 L O_2 exposure. With 100–1000 L exposures of O_2 most investigators report thin layers (<7 Å) of TiO_2 and other surface oxides (TiO, TiO_2O_3) have been suggested. At very low oxygen exposures it is possible to obtain a $p(2\times2)$ LEED pattern, which reverts to a (1×1) LEED pattern with additional oxygen exposure. Above 900 K, oxygen reportedly diffuses into the bulk. Removal of the oxide layer by ion bombardment during SIMS left a surface characteristic of the chemisorbed phase, and this oxygen was much more difficult to remove.[25] Similarly, the β phase had high stimulated desorption yields, while the α phase had low yields.[24]

Our experiments on the oxidation of Ti(0001) were very similar to those on Al(111): EELS spectra were taken for several different exposures at several different temperatures, before and after annealing the sample. At exposures of less than 1 L O_2 at 300 K, there is an oxygen induced loss peak at 65 meV (see Fig. 2) which must be the α phase. There is also a peak at 117 meV which appears after high temperature annealing and which disappears upon adsorption of oxygen, carbon, sulfur, or chlorine—the main contaminants in the crystal. It could be due to silicon diffused to the surface, since this is the only element present in the Auger spectrum which has a smaller peak to peak height after room temperature oxygen exposure. The 65 meV peak is observed when there is a $p(2\times2)$ LEED pattern, indicating that the β phase has not yet formed at 1/4 monolayer coverage. Further oxygen exposure at 300 K causes peaks at 40–45 meV and 90–92 meV to appear and grow in intensity, while the LEED pattern reverts to (1×1), indicating the β phase has begun forming. If the surface is sputtered after forming both the α and β phases of oxygen, the α phase alone remains. This is consistent with the SIMS and stimulated desorption results. If the surface is annealed above 500 K, the 91 meV peak disappears leaving the 65 meV peak, which also decreases in intensity with annealing above 900 K, consistent with oxygen diffusion into the bulk.

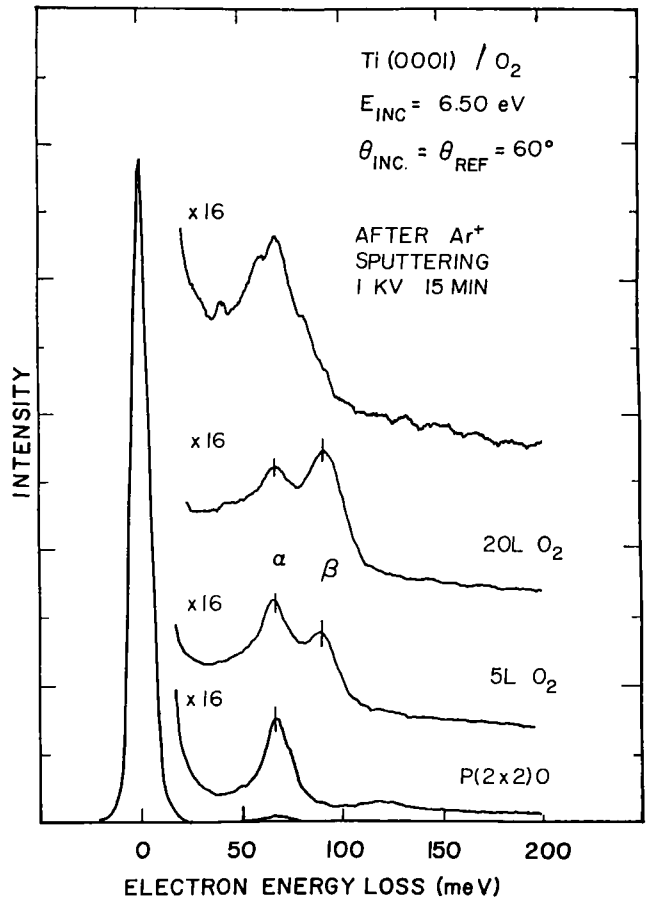

FIG. 2. EELS spectra for several doses of oxygen on Ti(0001) and after sputtering a surface following a 20 L dose.

If the titanium is exposed to oxygen at temperatures above 750 K only the 65 meV peak (the α phase) is present and the Auger spectrum never resembles that of TiO or TiO_2.[26] Similarly, large exposures at room temperature do not produce Auger spectra characteristic of the oxides, but now the EELS peak at 95 meV is the most intense. Exposure to 1000 L at 1.5×10^{-5} Torr at 600 K results in an Auger spectrum which resembles TiO as well as an argon ion bombarded TiO_2 crystal. Lo *et al.*[23] concluded that the surface oxide of Ti(0001) was, therefore, TiO_2 although they state that the sputtered TiO_2 is oxygen deficient, which would be consistent with formation of TiO. The EELS spectrum after 1000 L exposure under the above conditions now has the most intense peak at 86.5 meV (the β phase?) with a shoulder near 70 meV (the α phase). A dipole active mode at 95 meV has been observed on $TiO_2(100)$,[30] but this geometry would require substantial reconstruction of the Ti(0001) surface, which is inconsistent with the observed (1×1) LEED pattern. Infrared adsorption (transmission) spectra of TiO have absorption minima at 52.5, 59, 64, 97.5, and 135 meV.[31] The absorption minimum at 97.5 meV is weak while the minimum at 135 meV is the most pronounced. Neither of these

experiments can be correlated with our EELS data.

Removal of the β phase by sputtering would seem to indicate that this phase exists above the surface. If the oxygen diffuses into the crystal during annealing, the surface oxygen would necessarily be depleted. The α phase must have a higher binding energy than the β phase to explain the preferential removal of the β phase. The most appealing explanation is that the α phase is located below the surface. This would explain the work function, SIMS and stimulated desorption results. It is known from LEED[20] that nitrogen forms a (1×1) underlayer on Ti(0001) in the octahedral site before forming a nitrogen overlayer, so it would not be inconsistent for oxygen to behave similarly. In order to determine the adsorption geometry of either phase it will be necessary to perform off-specular EELS experiments to measure the oxygen vibrational modes parallel to the surface.

V. CONCLUSIONS

We have shown that EELS is a useful technique for probing chemisorption in which underlayer formation occurs. In cases where several modes can be detected as in the O/Al(111) system, lattice dynamical calculations can be used to investigate structural models. Even when several modes are not observable, experiments combining adsorption, annealing, and sputtering can provide enough information to identify modes corresponding to surface and subsurface species. The evolution of these modes as a function of dose and of temperature can provide insight into the kinetics of subsurface phase formation and changes in surface/subsurface concentration as a function of dose and temperature. EELS measurements of off-specular modes, and more generally the dispersion of the surface phonon bands along symmetry directions [as has been done for the O/Ni(100) system[27,32]] will provide the basis for a complete structure analysis of underlayer systems using lattice dynamical models.

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