ACID-SITE CHARACTERIZATION OF WATER-OXIDIZED ALUMINA FILMS BY NEAR-EDGE X-RAY ABSORPTION AND SOFT X-RAY PHOTOEMISSION

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ABSTRACT

Hydroxylated alumina films have been synthesized by water oxidation of single crystal Al(110) surfaces. Thermal dehydroxylation results in anion vacancies which produce an Al(3s) defect state 3.5 eV below the conduction band edge. A maximum in the defect-DOS occurs for oxides heated to 350 to 400 °C, which is where the materials exhibit maximum Lewis acidity with respect to C₂H₄. Adsorbed C₂H₄ produces thermally reactive C₂ species which interact covalently with the defect-DOS and nonbonding O(2p) from the top of the valence band. C(1s) binding energies suggest significant charge transfer which is consistent with a carbenium ion. Ni evaporated onto the surface, however, transfers charge directly to Al species and does not interact with O atoms at the defect site. The defect-DOS is regenerated when the C₂ species decomposes or when Ni migrates thermally through the oxide layer.

INTRODUCTION

Alumina films are widely used in corrosion inhibition, as dye receptors, as insulators, and as optical coatings. Usually, these films consist of either of amorphous alumina or of one of several "transition" aluminas. They are metastable phases which form depending on the hydrothermal history of the film¹. Amorphous alumina has primarily tetrahedral coordination while sapphire is octahedrally coordinated. Transition aluminas are characterized by varying ratios of tetrahedral to octahedral coordination. Some phases, *eg* γ and η , are poorly crystallized and have surface areas of several hundred m²/g, when they are prepared as bulk powders. These high surface area materials, which are usually synthesized from hydrous gels, are commonly employed as adsorbents, catalysts and catalyst supports. Surfaces of these materials are presumed to be terminated in hydroxyl (OH) groups. Such powders owe much of their rich surface chemistry to the presence of acid sites² which occur when the surface is partially dehydroxylated³. Though these reactive surface acids have been characterized by their chemical behavior⁴ and by infrared absorption⁵, little is known about their electronic structure. In this paper we report, for the first time, on the electronic structure of acidic defect sites in planar alumina films and the effects of basic adsorbates and metal deposits on that structure.

The electronic structure of alumina has been investigated intensely for many years. The apparent binding energy for the Al(2p) core level shows shifts of a few eV in x-ray photoemission spectra (XPS) for the different crystallographic forms but these shifts can be accounted for largely by charge transfer effects at the metal/insulator interface⁶ and by small extra-atomic relaxation shifts.⁷ The band gap has been found to be between 8.7 eV⁸ and 9.9 eV⁹. From a variety of measurements the valence band edge can be located *ca* 80 eV above the Al(2p) core level. An exciton *ca* 1 eV below the conduction band has also been observed in α -alumina.⁸⁻¹⁰

It has been suggested that surface acidity in aluminas results primarily from coordinatively unsaturated aluminum sites. Since some, if not the majority, of these acid sites function as Lewis acids, *i.e.* electron acceptors, it is possible that, electronically, they would produce empty

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defect states in the upper portion of the band gap. Such states would appear as pre-edge features in the soft x-ray absorption spectrum.

In this work we report on studies of soft x-ray photoemission (XPS) and absorption (XAS) on thin films, 20 to 50 Å thick, of alumina grown by water oxidation of single crystal Al(110). The films were then heated to various temperatures up to 500 °C. Water oxidation was used to maximize the incorporation of OH groups. The XPS and XAS measurements were made at NSLS on the U16B beamline, which is equipped with an extended range grasshopper monochromator (ERG). The use of synchrotron radiation in this work makes it possible to complete the equivalent of ultraviolet photoelectron spectroscopy (UPS), XPS, and XAS on a single sample with a carefully controlled preparation. All of the photoemission spectroscopy can be carried out with photoelectrons which have the same range of kinetic energies. This means that they sample the same portion of the material. The ERG monochromator has excellent transmission at the energies required for Al(2p), C(1s), and O(1s) spectroscopies. The use of thin films gives an internal calibration of all binding energies by referencing them with respect to the known binding energy Al-metal.

RESULTS AND DISCUSSION

All the films were prepared by oxidation of Al(110) surfaces with water at room temperature and then rapidly heated (flashed) to a selected temperature (≤ 500 °C) and quenched. XPS and XAS measurements were then taken at room temperature. The XPS data were acquired with a cylindrical mirror analyzer and the XAS were obtained using total electron yield.

The results of the XPS measurements have been described in detail elsewhere¹¹ but will be summarized briefly here. As the treatment temperature increased, the OH-content of the films decreased monotonically and the degree of crystallinity increased monotonically. Adsorption of ethylene, a weak Lewis base (electron donor), produced a binding energy shift of +2.8 eV in the O(1s) core level for a portion of the oxygen species but no measurable shift in the Al(2p) level. The intensity of the shifted oxygen species passes through a maximum for materials flashed to temperatures between 350 and 400 °C. The valence band spectra show that whatever molecular fragments are present still retain the C₂ structure of ethylene. The ethylene-derived valence band states are consistent with the presence of a ⁺C₂H₅, a carbenium ion. Carbenium ions are known to be a very reactive intermediates². This expectation was corroborated when the surface was warmed rapidly from 120 K to 210 K and then quenched. Such treatments removed all traces of the C₂ species but resulted in little change in the total amount of carbon on the surface.

Alumina Films

The absorption spectra for films produced at room temperature and subsequently flashed to higher temperatures, up to 500°C, are shown in figure 1 for absorption about the Al(2p) edge. The intensities of the total electron yields are plotted as a function of the energy of the incident photon. In all of the spectra, there is a small but distinctive feature near 72.5 eV which results from the aluminum metal substrate, *i.e.* the 2p edge. There is some incorporation of metallic aluminum in nearly all UHV-grown oxides, either as a result of a nonplanar metal/oxide interface or as small metal crystallites within the oxide matrix.^{12,13} The Fermi edge of Al-metal is also evident in the valence band spectra of these materials.¹¹ The splitting due to spin-orbit coupling is observed in the metal edges shown in figure 1. XPS binding energies for Al-metal are 72.5 and 72.9 eV for the two spin states, which coincides with the splitting shown at the metal edges in figure 1.¹⁴

The rest of the features are attributed to electron transitions in the oxide. Peaks at 76.5, 80.0 and 83.4 eV are present in all of the films. An additional feature between 78 and 79 eV is seen in the oxides flashed to temperatures above 400 °C but absent those treated at lower temperatures. The feature at 80.0 eV is the main absorption edge and coincides with excitation

from Al(2p) into the lower part of the conduction band. Subtracting 71.3, the measured Al(2p) binding energy with respect to the valence band edge gives 8.7 eV for the band gap which is equal to that reported from optical reflectance measurements on sapphire.⁹ Following Balzarotti *et al*¹⁵ the main edge, 80.0 eV, is assigned to the Al(2p)→Al(3s) transition and the 83.4 peak to Al(2p)→Al(3d). The remaining features in figure 3 have final state energies that lie within the gap and their assignments are more tentative. The 78.8 eV feature in the oxides flashed to above 400°C is attributed to an exciton by analogy to that found in α alumina.⁸⁻¹⁰ The exciton is not present in the room temperature oxide, first appears at 78.3 eV in the material flashed to 425°C, and then grows in intensity with temperature until it overshadows the Al(2p)→Al(3s) peak.

The more prominent and pervasive feature within the gap is the one at 76.5 eV, which is 3.5 eV below the conduction band edge. This energy is three times the binding energy of the exciton observed for α -alumina and has a density of states (DOS) that is distinct with respect to the observed exciton, which has a binding energy similar to that of the exciton in α -alumina. We therefore assign this feature to a geometric defect. At these treatment temperatures one would expect to find small crystallites of γ -alumina in a matrix of amorphous material.¹¹ Such a material would have myriads of defects some of which could be expected to produce states within the gap. The intensity of this defect state passes through a maximum for materials flashed to temperatures of 350 to 400 °C, which is the temperature range at which the materials show their maximum Lewis acidity with respect to ethylene.¹¹

Tight-binding band structure calculations¹⁶ and cluster calculations¹⁷ on α -alumina all show defect states within the band gap either for Al-terminated surfaces or for O-terminated surfaces with anion vacancies. All the calculations exhibit an Al(3s,p_z) DOS which has dropped below the bottom of the conduction band and a destabilization of O(2p)-DOS near the top of the valence band. A defect state 4 eV below the conduction band has been identified in electron loss spectroscopy (ELS) on the (1012) surface.¹⁸ ELS spectra from reconstructed and ion-bombarded (0001) surfaces also exhibit empty states within the band gap.¹⁹ While none of these electronic structure calculations can be applied directly to transition aluminas, the defect-DOS they reveal within the band gap and the experimental observations of defect-DOS add credence to our assignment of the 76.5 eV peak to a defect state. The dipole selection rule implies that the defect-DOS in figure 1 has primarily s-character and can therefore be attributed to Al(3s). XAS spectra at the oxygen edge show no pre-edge features for any of the films studied. In contrast to the calculations on α -alumina, this indicates little Al(3p) contribution to the defect-DOS. No electronic structure calculations have been reported for geometries which represent transition aluminas and no defect states have been previously identified experimentally in the transition aluminas.

Adsorbates: Ethylene and Nickel

Adsorption and/or deposition of Lewis bases (electron donors) would be expected to produce strong interactions with these defect states. Figure 2 shows the effects of surface species resulting from ethylene adsorption. The defect-DOS is shown for a film flashed to 350 °C, which, as mentioned earlier, produces a maximum in the defect-DOS. Spectra are shown prior to ethylene adsorption, after adsorption at 120 K, and after warming to 210 K. Recall that surfaces flashed to 210 K result in decomposition of C₂ species. When ethylene is adsorbed, the intensity of the defect-DOS decreases and the intensity of the DOS at the bottom of the conduction band increases. This is accompanied by a sharp decrease in the DOS at the valence band edge¹¹, which suggests stabilization of the O(2p) states which reside there. Further evidence for the involvement of oxygen in the bonding comes from the increase in the apparent binding energy of O(1s). This shift is similar to that found for OH-groups and probably results, in both cases, from a final state effect rather than a significant charge transfer from oxygen to hydrogen. It does suggest, however, a strong interaction between oxygen and the hydrogen in the C-H groups of the C₂ species. There is no significant shift in the Al(2p) binding energy but the C(1s) core levels show a large shift, *ca* +4 eV, which is consistent with a carbenium ion like ⁺C₂H₅.

Transition metals can be either electron donors or acceptors. Metals late in the period, *eg* Ni, Pd, and Pt should be stronger Lewis bases (electron donors) than the early members. With this in mind, Ni was deposited at 90 K on alumina films prepared to have maximum Lewis acidity. The total-yield-XAS is shown in figure 3 for deposition of 3 equivalent monolayers of nickel. Also present is a spectrum from the oxide layer prior to Ni deposition. When nickel is deposited, the Ni(3p) edge appears prominently in the XAS and all of the oxide features are attenuated, but the ratio of the Al(3s) defect to the Al⁰ edge decreases by a factor of 2~~3~~. As the treatment temperature increases and the Ni eventually migrates through the oxide layer into the bulk,²⁰ the intensity of the defect-state is regenerated and that of the nickel edge decreases. Like ethylene, Ni interacts strongly with the acid site. Unlike ethylene, however, there is no appreciable gain in the intensity of the DOS near the bottom of the conduction band. This probably indicates that the interaction with Ni broadens and/or destabilizes the Al(3s) much more than the ethylene interaction does. There are other important differences in the Ni-interaction compared to ethylene. Nickel produces no shifts in the O(1s) binding energy but there is a shift of +0.8 eV in Ni (3p) indicating significant charge transfer to the acid site as expected. This results in a shift of -1.3 eV for the Al(2p) level. Charge transfer to the oxide should decrease the amount of band bending which would increase the apparent binding energy; thus the -1.3 eV value represents the net difference between these two effects.

Using synchrotron radiation for this work has provided information about these acidic defects in alumina in unprecedented detail. We have been able to identify their energy unambiguously and their orbital symmetry. We have shown how these specific defects interact electronically in strong chemical reactions with a hydrocarbon molecule and a transition metal, identifying details about the nature of the bonding modes. This probably represents the first characterization of the electronic structure of solid acids in such detail.

Conclusions

Both ethylene and nickel interact strongly with acidic Al(3s) defect-states which occur as a result of dehydroxylation of the surface. While Ni interacts primarily with Al(3s)-states and transfers charge to the aluminum center, ethylene interacts strongly also with the oxygen species and has primarily covalent interactions with Al(3s). The defect sites are regenerated when the ethylene-derived C₂-species decompose or when Ni migrates through the oxide into the bulk. These measurements represent the first direct characterization of chemically active acid sites on alumina.

ACKNOWLEDGEMENT

Primary support was provided by the Mobil Research and Development Corporation. Additional support came from the Cornell Materials Science Center under NSF Grant DMR16616-AO2 and from DOE-BES (Material Sciences) under Contract ACO4-94AL85000 with Sandia National Laboratories. Measurements were conducted at the National Synchrotron Light Source, Brookhaven National Laboratories, Upton, NY 11973, which is supported by the Office of Basic Energy Sciences, United States Department of Energy, under Contract DE-ACO2-76CH00016.

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Figure 1: Al L₂₃ Edge Total Electron Yield Spectra for Heat Treated Alumina Films.

Figure 2: X-ray Absorption Spectra for a) 673K Heat Treated Film, b) 673K Film after Ethylene Exposure, c) After Warming the Ethylene Dosed Film to 210K.

Figure 3: Total Electron Yield Near Edge Spectra for a 3 ML Nickel Film