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Al-Al_2O_3 interface study using surface soft-x-ray absorption and photoemission spectroscopy

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The local structure and the electronic states of a thin oxide layer on a single-crystal Al (111) surface has been studied using surface soft-x-ray absorption and soft-x-ray photoemission spectroscopy. Unoccupied interface states are found in the oxide band gap. The local structure of the thin oxide layer is compared with the structure of bulk Al_2O_3. The effect on the electronic states of an amorphous to crystalline phase transition is shown. The crystalline oxide-metal interface has fewer unoccupied interface states in the Al_2O_3 gap than the amorphous oxide-metal interface.

I. INTRODUCTION

The electronic structure of the first few monolayers of oxide grown on the Al (111) single-crystal surface exposed to molecular oxygen has been investigated using surface-sensitive electron spectroscopies. These include both photoemission and surface absorption measurements. The surface soft-x-ray absorption spectra (SSXA) were measured using partial-yield spectroscopy with the final-state energy E^* set to the 45-eV Auger electrons from the valence-band (VB) interatomic Auger process Al-$2p$-O-$2s$.[1] The surface $L_{2,3}$ photoabsorption cross section is thus obtained from a surface layer defined by an effective escape depth $l(E^*)$ of approximately 2 Å,[2] for 45-eV electrons. Soft-x-ray absorption spectroscopy (SXA) is a sensitive probe of the local structure around the absorbing atom.[3,4] The near-threshold SXA spectrum of an insulator within about 50 eV of threshold is determined both by molecular excited states, "inner-well states"[4] or "shape resonances"[5] because of the localized initial state and by extended states of the solid. The local symmetry, the nature, and the electronegativity of the atoms surrounding the absorbing atom determine the shape of the SXA spectrum. Complementary valence-band and $2p$ core-level information has been obtained with soft-x-ray photoemission spectroscopy. The exciting-photon energy in each case is selected so that the photoelectron final-state energies are in the range 30–50 eV. This minimizes the effective escape depth so that the surface is emphasized.

The measurements discussed here show that unoccupied states occurring in the Al_2O_3 gap are related to an intermediate Al oxidation state. Such states are correlated to the Al-Al_2O_3 interface states which lower the conduction-band edge in the oxide-semiconductor transition layer. Such a lowering of the conduction-band edge in the metal-oxide transition region has been found by electron-tunnelling experiments[6] performed with a thin (~100 Å) insulating oxide layer. The tunnelling experiments have shown an asymmetric potential barrier[7-12] and it was suggested that an excess of Al atoms will create energy levels in the Al_2O_3 band gap lowering the conduction band in a transition region approximately 10 Å thick between the metal and the oxide. This led to the hypothesis of the existence of a semiconductor-like phase of the oxide at the metal-insulator interface.[7]

The paper proceeds as follows. After a discussion of experimental technique in Sec. II, the results are presented in Sec. III. Section III is divided between the photoemission and absorption results. The results are discussed in Sec. IV.

II. EXPERIMENTAL

The experiments were performed on the 4° beam line[13] at the Stanform Synchrotron Radiation Laboratory (SSRL) using monochromatized synchrotron radiation emitted by the storage ring SPEAR. The samples were high-purity electrolytically polished single crystals of aluminum. Electron microscopy subsequent to the measurement showed the (111) surface used to have a very low defect density. The initial surface was cleaned *in situ* by successive argon sputtering and annealing. For photoemission spectroscopy, p-polarized photons have been used with energies of 50 and 130 eV to measure the electron energy distribution curves (EDC) of the valence band and of the $2p$ core levels, respectively. The photoemitted electrons have been energy analyzed by a double pass cylindrical mirror analyzer with a resolution of 0.4 and 0.2 eV for the valence and for the core spectra, respectively. Surface photoyield measurements with both high and low final-state energies have been used to determine surface absorption coefficients with different sampling depths.[1] With the constant final state energy set for 45 eV corresponding to the Al-$2p$-O-$2s$ valence-band interatomic Auger transition, the cross sections of the inner shell transitions occurring within a thin surface layer about two times the effective escape depth 2 Å thick is measured and the surface aluminum atoms bonded to oxygen atoms are emphasized. The partial yield spectra presented are normalized to the incidence photon flux.

The clean Al(111) surface was exposed to 100 L of oxygen (1 langmuir = 10^{-6} Torr sec) to get approximately a monolayer of oxygen chemisorbed on the surface.[14-16] To grow a 5-Å-thick oxide layer, the sample was exposed to 10^6-L O.[17] The oxidation of aluminum with molecular oxygen exposure is slow[8] and a 20 min exposure to air at room temperature is necessary to grow a stable 25–30-Å thick oxide layer.[6,17] The measurements reported were made at room temperature, and after heating the sample to 200 and 400 °C. It is well known that in a 30-Å-thick oxide layer, a phase transition occurs at 350 °C from amorphous to γ alumina. Such a transition is found in this work in going from 200 to 400 °C.

III. RESULTS

A. Soft-x-ray photoemission

Figure 1 shows the valence band photoelectron energy distribution curves (EDC) of Al_2O_3 grown on the Al(111) surface by exposing it to 10^6 L of oxygen at room temperature and then annealing at 400 °C. Two maxima in the Al_2O_3 valence band are observed at room temperature at −7.6 and −11.2 eV below the Fermi level. The features have a higher binding energy then the corresponding peaks observed at lower oxygen exposure.[22] These structures have been observed in bulk Al_2O_3 at 68.2 and 64.2 eV above the $2p$ core level.[18] Using the calculations for bulk alumina,[19] the structure at −7.6 eV should be assigned to nonbonding $2p$ lone pair orbitals and the structure at −11.2 eV to the hybridized oxygen sp^2 orbitals mixed with the aluminum sp^3 orbitals. Above the amorphous to crystalline phase transition temperature at 400 °C, the −11.2-eV initial state peak shifts toward higher binding energy so the energy splitting of the two peaks becomes 4 eV and is comparable to γ-Al_2O_3. Also an increase of its intensity indicates a change in the electronic structure of the oxide when heated above 350 °C.

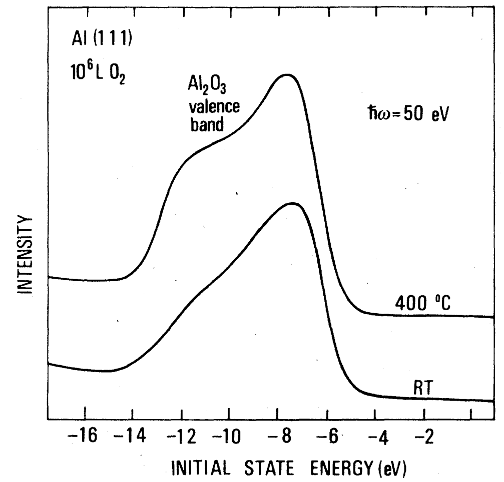

FIG. 1. Photoemission spectrum, using 50-eV photon energy, of the valence band of Al_2O_3 grown on the (111) surface of an Al single crystal exposed to 10^6 L of oxygen. The spectrum of the crystalline oxide was obtained by heating the sample to 400 °C.

Figure 2 shows the EDC's of the Al $2p$ core levels. At room temperature the intensity ratio R of the Al^{3+}-$2p$ peak relative to that of the Al-$2p$ is about 4. Assuming that the photoionization cross section at $\hbar\omega = 130$ eV (Ref. 20) and the escape depths $l(E^*)$ in the aluminum and in the oxide[9] are the same, the thickness $d = 5$ Å of the oxide layer has been qualitatively estimated by the formula $d = l(E^*)\ln(R+1)$.

The aluminum spin-orbit-split $2p$ core levels are centered at 73 eV below the aluminum Fermi energy and the core level in the oxide Al^{3+} $2p$ at room temperature is at 75.8 eV. After heating the sample at 400 °C it shifts to 76.3 eV with a chemical shift of 3.3 eV compared to the 2.7-eV chemical shift of the bulk oxide.[21] Heating at

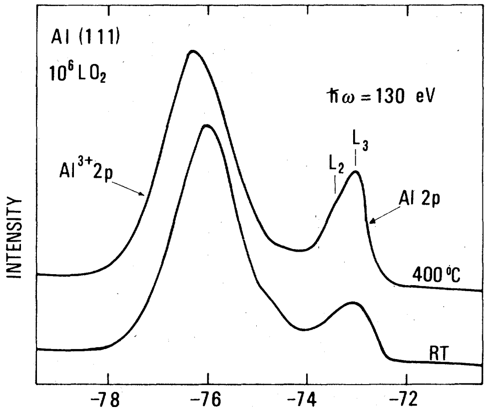

FIG. 2. Photoemission spectrum, using 130-eV photon energy, of the $2p$ core levels of aluminum and of Al_2O_3. The Al (111) single crystal was exposed to 10^6 L of oxygen to get a 5-Å-thick oxide.

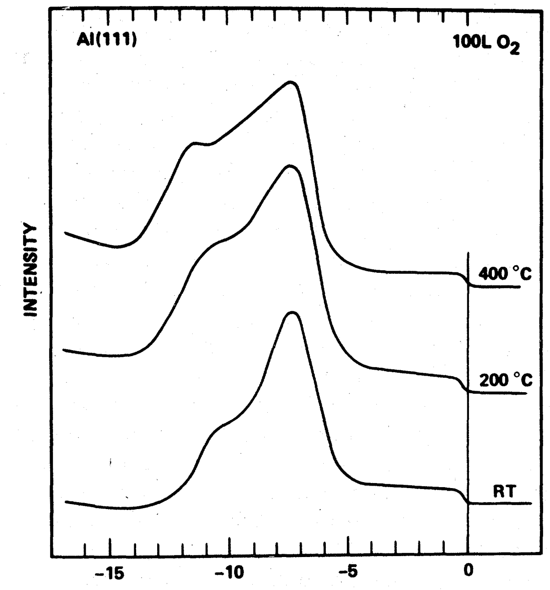

FIG. 3. EDC of the oxygen-induced states in the aluminum valence band of the Al(111) crystal exposed to 100 L of oxygen. The effect of the temperature is discussed in the text.

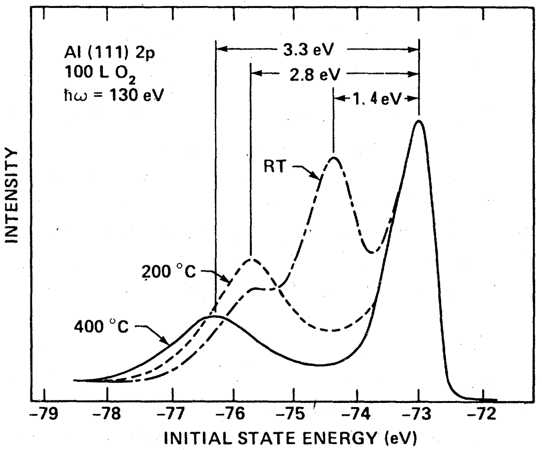

FIG. 4. EDC of the Al-2p core level, of the 1.4-eV chemically shifted Al* 2p, and of the Al^{3+}-2p levels for an Al(111) surface exposed to 100 L of oxygen. The change of the chemical shift with temperature is shown.

400 °C increases the relative intensity of the Al-2p peak which could indicate that crystalline oxide clusters form with some islands of clean aluminum surface exposed, although other possibilities exist.

The same transition to a crystalline phase also occurs for a monolayer of chemisorbed oxygen on the Al surface. By exposing a clean room temperature Al(111) surface to 100 L of oxygen, a monolayer of chemisorbed oxygen atoms forms outside the surface.[14,22] Figure 3 shows the resulting EDC of the oxygen induced levels in the valence band. This is in good agreement with the calculation of a two-dimensional band structure of a monolayer of oxygen chemisorbed on the Al surface.[23] These states originate from the O 2p orbitals parallel to the surface. By heating to 200 °C the valence band becomes broader, 8.8 eV wide, like that on the 10^6-L-exposed surface, showing the formation of the oxide. But in this case because of the limited amount of oxygen, the oxide must be in clusters. In the EDC of the core levels shown in Fig. 4, the 1.4-eV Al*-2p core-level shift[15] due to the intermediate oxidation state of the aluminum atom interacting with the chemisorbed oxygen is observed at room temperature. At 200 °C the intermediate oxidation state disappears[16] accompanied by oxide formation and only the 2.8-eV shifted peak characteristic of the oxide remains. By heating to 400 °C, the same phase transition observed in the 5-Å-thick oxide, is seen. The formation of clusters of crystalline oxide is characterized by the changes in the valence band in Fig. 3. The al^{3+}-2p core-level shifts to 3.3 eV from the aluminum 2p level and the relative increase of the intensity of the Al-2p peak show the increase of the relative area of clean aluminum on the surface.

B. Surface soft-x-ray absorption spectra

1. *Initial thick oxide*

We first discuss the spectrum of the ~5-Å-thick oxide grown on the Al(111) surface exposed to 10^6-

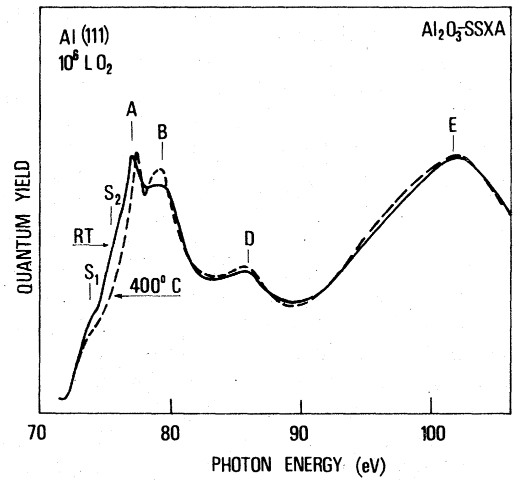

FIG. 5. $L_{2,3}$ surface soft-x-ray absorption spectrum measured by using the interatomic Auger yield technique. The aluminum surface was exposed to 10^6 L of oxygen to get a 5-Å-thick oxide layer. Only core transitions into the thin oxide layer contribute to the spectrum. The dashed curve is the spectrum of the crystalline oxide formed by heating the sample at 400 °C.

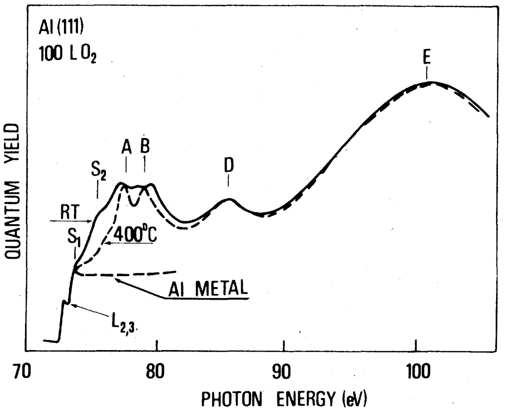

FIG. 6. $L_{2,3}$ surface soft-x-ray absorption spectrum of the Al(111) surface exposed to 100 L of oxygen. The contribution to the spectrum due to the aluminum metal substrate is shown. The spectrum of the crystalline oxide formed by heating the sample at 400 °C is plotted (dashed curve).

L O_2. Figure 5 shows the surface soft-x-ray absorption spectrum obtained by the measurement of the quantum yield of the interatomic Auger electrons (IAYS)[1] plus the inelastic background. The threshold of the Al-2p core transitions, at 73 eV, does not show a sharp metallic edge and the photoionization cross section increases slowly up to 77 eV. This distribution of the oscillator strength is not typical of a metal such as Aluminum with a sharp edge at 72.72 eV.[20] Neither is this typical of a large gap insulator such as bulk Al_2O_3 which has the threshold T_0 of the $L_{2,3}$ photoabsorption at 76.3 eV,[20] and sharp peaks near the edge. A similar shape of the Al $L_{2,3}$ edge was observed for dilute Al atoms in alloys.[24]

The SSXA spectra in Figs. 5-7 exhibit two broad structures S_1 and S_2 in the range 73-76.3 eV which are not present in the SXA spectra of either bulk aluminum or bulk Al_2O_3.[20] By joint core level photoemission and SSXA spectra, the initial and final states of these transitions can be determined. The EDC data of the 10^6-L-exposed sample show two possible initial states: the Al^{3+}-2p level in the oxide and the Al-2p level in the metal. From the Fermi level position in the metal, one can define a minimum possible threshold energy of core transitions. The Al^{3+} 2p level is known from the photoemission data to be at 75.8 eV below the Fermi energy, therefore no optical transitions from this level are allowed for $\hbar\omega < 75.8$ eV. The transitions between 73- and 75.8-eV photon energies should be assigned to the Al-2p initial state. Since the bulk SSXA spectrum of clean aluminum has no structure in this energy range, as can be observed in Fig. 6, these structures in the SSXA spectrum should be assigned to interface states.

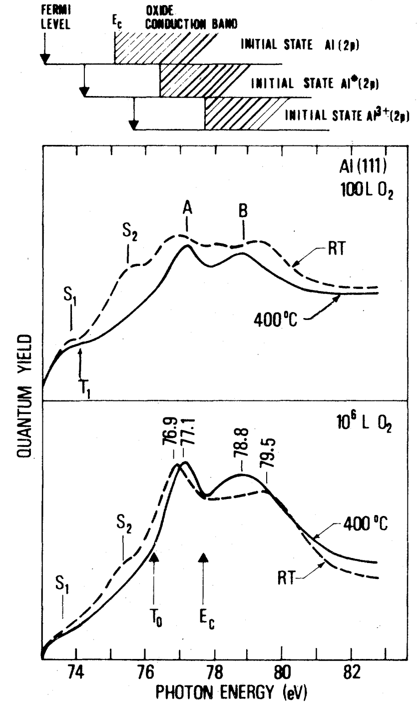

FIG. 7. Surface soft-x-ray absorption spectra above the Al $L_{2,3}$ edge are shown. T_0 is the threshold of photoabsorption in bulk oxide; E_c is the bottom of the conduction band in Al_2O_3. The spectra at room temperature (RT) and above the amorphous to crystalline phase transition (400 °C) are plotted. The energies of the core transitions to the final states E_F and E_c from the initial states (Al 2p of aluminum, Al* 2p of the intermediate oxidation state, Al^{3+} 2p of the oxide) are shown in the upper part of the figure.

The structure S_1 is assigned to a transition from the Al-2p level to a band of interface states above the Fermi energy. These states are in the Al_2O_3 gap since the conduction band edge of Al_2O_3, E_c, is located 2 eV above the Fermi energy, i.e., 75 eV above the Al-2p level. (The height of the Al-Al_2O_3 potential barrier $\varphi = 2$ eV has been measured by tunnelling experiments.[6-12]) The transition S_1 to the interface states is localized on aluminum atoms at the metal-oxide interface. These atoms can also be impurities in the oxide or part of Al-like microscopic clusters mixed in the oxide. In this case a nonstoichiometric oxide transition region should be present at the Al-Al_2O_3 interface. This hypothesis suggests the existence of an aluminum rich semiconducting Al_2O_3 phase in the transition region. The interface states can be identified as the donor-type energy levels suggested by Fisher and Giavert[6,7] which result in the band gap lowering with the conducting band edge 0.2 eV above the Fermi energy in the Al_2O_3 oxide transition region at the interface.

2. *Initial monolayer of oxygen*

Figure 6 shows the soft x-ray absorption spectra of the Al(111) surface exposed to 100 L of oxygen at room temperature and after heating the sample to 400 °C. At this exposure at room temperature there is approximately a monolayer of chemisorbed oxygen on the surface.[14-16] The shape of the $L_{2,3}$ edge of the aluminum metal at 72.72 eV is clearly observed. The spectra are normalized so that the $L_{2,3}$ edge overlaps the $L_{2,3}$ edge of the bulk Al metal spectrum. The contribution of the inner shell transitions localized within the metal substrate can be subtracted. We have assigned the oxygen induced structure S_2 and the broad band from 73 to 82 eV to transitions from the Al*-2p level to extrinsic surface states. At room temperature the 1.4-eV chemically shifted peak, Al*-2p, is clearly observed in Fig. 4. Optical transitions from this state are allowed for $\hbar\omega > 74.4$ eV (see Fig. 7). Above the amorphous to crystalline phase transition temperature, the structure S_2 disappears as does the 1.4-eV chemically shifted peak in Fig. 4. This strongly supports the assignment of the S_2 structure to a transition from the Al*-2p level. This transition is associated with the intermediate oxidation state induced by chemisorbed oxygen and it should be expected also at the Al-Al_2O_3 interface. In fact, the S_2 peak is observed also in the 10^6 L exposed Al surface when the first oxide monolayer of the Al-Al_2O_3 interface is formed. In this case the final states of the S_1 and S_2 transitions are unoccupied interface states. As can be seen in Fig. 7 after annealing at 400 °C, both the S_1 and S_2 structure due to transitions to interface states become weak. This effect suggests a decrease of the interface states at the metal-crystalline oxide interface. This microscopic phenomena should be correlated with the effect of the annealing above 400 °C on the electrical tunnelling characteristics through the Al-Al_2O_3 interface.[6,7]

IV. DISCUSSION

The transitions discussed can be understood with the help of Fig. 8 which presents an energy scheme of the Al-Al_2O_3 electronic states obtained from the photoemission data for the sample exposed to 10^6 L at room temperature. The arrows indicate the core electronic transitions observed in the SSXA spectra in Fig. 7. Structures in the energy range 73–76 eV have been observed in SXA of aluminum films exposed to air with a ~25-Å-thick oxide layer.[25] They have to be assigned to interface states as the S_1 and S_2 structures.

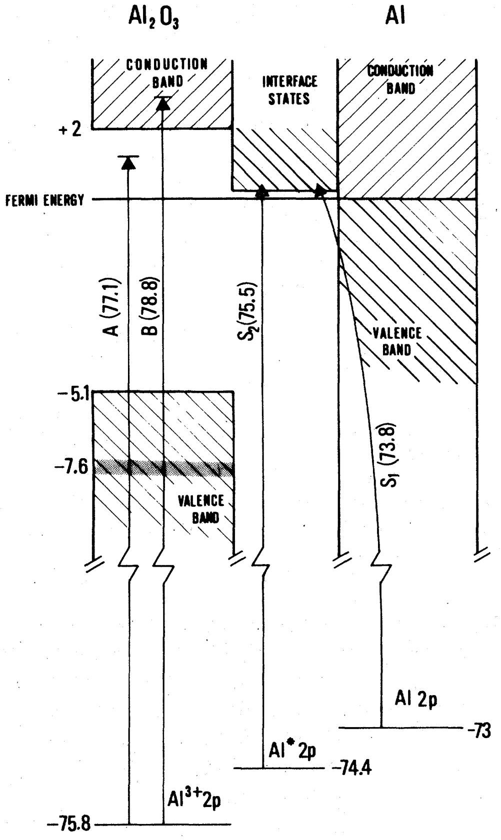

FIG. 8. Energy scheme of Al and Al_2O_3 electronic states of our sample with a 5-Å-thick oxide layer. The energies, obtained by photoemission data, are in electron volts and the error is about ±0.1 eV. The arrows indicate the core transitions in the SSXA spectra.

We now compare the structures A, B, and E at higher energy in Fig. 5 with the bulk Al_2O_3 $L_{2,3}$ soft-x-ray absorption spectrum.[20] Following Dehmer,[4] the strong peaks at the edge of the $L_{2,3}$ spectrum of an atom surrounded by electronegative ions should be assigned to inner well states located near the potential barrier due to the electronegative ions. These transitions are essentially localized in the Al_2O_3 molecule so they bring information on the local Al-O bonding. In a tetrahedral environment,[26] the expected inner well states are a_1 (s-like), t_2 (p-like), e and t_2 (d-like). We assign the peak A to the a_1 state. The peak A in fact corresponds to the 2p-3s transition in the Al^{3+} ion. As can be seen in Fig. 8, it is a discrete inner well state. Considering it as a core exciton, its radius is shorter than the Al-O distance so the excited well function is essentially atomic.[1] The peak B has no corresponding atomic transition so it should be assigned to an excited molecular state, like that predicted by Dehmer, t_2 (p-like).

In agreement with this assignment, the core transition from the 1s level to the same final state[27] has a strong oscillator strength showing that this final state has a mixed p and s symmetry. Finally the peak E is assigned to a d-like final state since it is not observed in the electronic transitions from the 1s level.[27]

The main difference between the bulk amorphous Al_2O_3 $L_{2,3}$ spectrum[20] and the spectrum in Fig. 5 of the thin oxide layer in this energy range is the decrease of the intensity of the peak B and the shift of peak E to higher energy. The peak A is essentially atomic so no changes are expected. The oscillator strength change of t_2 (p-like) and the shift of the t_2 (d-like) inner well excitations suggest that different Al-O bonding occurs in the thin oxide layer. The presence of aluminum impurities and a different site symmetry around the absorbing atom, lowering the electronegative potential barrier due to the O ions, can produce the effects observed on the excited molecular states.

By heating at 400 °C, the peaks A and B of the oxide monolayer shift in the same way and to the same energies as seen from the phase transition from amorphous to γ alumina.[20] This effect suggests that the structure of the crystalline phase of the oxide monolayer is closely related to that of the γ-Al_2O_3. The shift of the peak A toward higher energy in the crystalline oxide is due to the higher binding energy of the Al^{3+}-2p level in crystalline oxide as can be seen in Fig. 2.

V. CONCLUSION

Evidence of unoccupied interface states at the Al-Al_2O_3 interface has been presented using surface soft x-ray absorption spectroscopy. The states have been correlated with the semiconducting phase of the transition oxide layer at the Al-Al_2O_3 interface.

A comparison of the oxide SSXA spectrum with bulk Al_2O_3 SXA spectrum has indicated small variations in the local structure of the oxide monolayer. Above the amorphous to crystalline oxide phase transitions temperature (~350 °C) the shape of the valence band and of the core-level photoemission spectra changes. The density of interface states decreases strongly at the metal-crystalline oxide interface. The Al^{3+}-2p core level shows a different chemical shift from the thick oxide. The amorphous to crystalline phase transition has been characterized.

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