The electronic structure of ultrathin aluminum oxide film grown on FeAl(110): A photoemission spectroscopy

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The electronic structure of the ultrathin aluminum oxide grown on the FeAl(110) surface has been investigated with angle-resolved photoemission spectroscopy. Previous scanning tunneling microscopy studies have revealed that exposing the clean FeAl(110) surface to 1000 l of oxygen at 850 °C forms a homogeneous hexagonal oxide film with a thickness of approximately 10 Å. Core level photoemission spectra of FeAl constituents indicate that Al is the only metal species present in the oxide film. The measured band dispersion of the oxide thin film indicates a two dimensional electronic structure parallel to the plane of the thin film due to the limited thickness of the oxide thin films. The appearance of a peak in the anticipated band gap of the bulk oxide film suggests a unique electronic structure of the two dimensional oxide film. This latter observation is correlated with previous scanning tunneling microscopy results to elucidate the structure of the ultrathin alumina film grown on FeAl(110). © 2007 American Institute of Physics. [DOI: 10.1063/1.2710305]

I. INTRODUCTION

Thin-film oxides have received considerable attention due to their applications in many technological fields from metal-based sensors to catalysis. Particularly, in catalysis, the atomic and electronic properties of the oxide surface play an essential role to enhance or diminish the catalytic activity. In the last decades, studies have focused on understanding and controlling these properties. However, the complex atomic and electronic structures, charging problems, and poor electrical and thermal conductivities of bulk oxides have limited the understanding of their fundamental properties. These experimental difficulties have been minimized by the growth of ultrathin oxide thin films on well-characterized metal substrates, which have been model systems to study the surface properties of bulk oxides.

Thin oxide films grown on NiAl alloys have been the subject of many previous studies due to their particular importance in technological applications such as corrosion protection at high temperatures for coatings such as those on turbine blades in jet engines and because they provide an appropriate representation of model catalyst supports. Scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED) studies have proved that a well ordered 5 Å thick γ-Al2O3 film is formed on NiAl(110) after dosing 1200 l of O2 at elevated temperatures and subsequent annealing to 850–950 °C for a short time. Two layers of oxygen and aluminum ions were proposed in the epitaxially grown ultrathin oxide. Libuda et al. have asserted that this oxide has γ-Al2O3-like rather than α-Al2O3-like structure, and is terminated with a hexagonal arrangement of oxygen ions by the use of high-resolution electron energy-loss spectroscopy (HREELS) technique. In addition, a mixture of octahedral and tetrahedral Al ions similar to γ-Al2O3 structure was proposed.

FeAl is also an ordered transition metal alloy, like NiAl, and possesses the same crystal structure CsCl type. The oxidation behavior of FeAl(110) has not been studied in detail, in contrast to NiAl transition alloy. Employing Auger electron spectroscopy (AES) and (LEED), Graupner et al. reported that the oxidation of FeAl(110) surface at elevated temperatures gives rise to a well ordered oxide film with a thickness of 6 Å. In a previous paper from our group, a STM study of oxidation behavior on FeAl(110) has been presented. In order to corroborate the morphology reported therein, in the present paper, we discuss and report our angle-resolved photoemission spectroscopy (ARPES) measurements to better reveal the nature and dimensionality behavior of the electronic structure of the oxide thin film on FeAl(110).

II. EXPERIMENTAL DETAILS

STM and ARPES measurements were performed at the Center for Advanced Microstructures and Devices (CAMD) at Louisiana State University. A VSW HA150 hemispherical electron energy analyzer on the endstation of the 6-m toroidal grating monochromator (TGM) beamline was used for...
ARPES measurements. \( s+p \) polarized light was implemented with a 45° incident angle for normal emission measurements. Since the hemispherical analyzer is fixed, the crystal was rotated for off-angle measurements. The detailed description of the STM imaging and the sample preparation for STM studies can be obtained in Ref. 6. For ARPES measurements, the sample was placed on a 2 × 2 cm\(^2\) Ta sheet with two W wires passing through the sides of the crystal, which resistively heated by passing the current through the W wires. The substrate was cleaned by repeated cycles of sputtering at room temperature.

The substrate was cleaned by repeated cycles of sputtering at room temperature with two W wires passing through the sides of the crystal, which resistively heated by passing the current through the W wires. The ultra-thin oxide films on FeAl surfaces were prepared by dosing the sample with oxygen at 850 °C and consequently annealing for 5 min at this temperature.

III. RESULTS AND DISCUSSION

Not surprisingly, there have been more studies to probe the atomic structure of the thin oxide films grown on transition metals compared to those studies on their electronic structures. Due to their well studied clean surfaces, among the transition metal aluminides, Ni based transition metal aluminides have been studied intensively to reveal the electronic structure of the thin oxide film. Graupner et al. reported the first detailed electronic structure study to elucidate the nature of the Al\(_2\)O\(_3\)/NiAl(100) system by using XPS and ARPES.\(^5\) XPS measurements revealed that exposing the clean surface to oxygen at elevated temperatures chemically affects Al atoms and not Ni. In addition, the XPS results found higher binding energy features in the oxide overlayer on NiAl(110) and asserted that both tetrahedrally and octahedrally coordinated Al ions exist in the oxide film. The ARPES measurements utilizing both \( s \)- and \( p \)-polarized light exhibited a well defined two dimensional band structure parallel to the surface.

Although FeAl shares the same crystal structure with NiAl, there have been no studies to detail the electronic structure of an oxide film grown on FeAl(110). Here, upon shortly detailing the morphology of the oxide film formed on FeAl(110), we will discuss ARPES findings to reveal the electronic behavior of the film.

As detailed in our previous study,\(^7\) the clean surface of FeAl(110) exhibits surface reconstructions. The preferential sputtering results in an attenuated Al concentration in the near surface region; however, annealing this surface promotes a diffusion of Al atoms to the surface selvage region. At temperatures above 800 °C, an incommensurate phase occurs on the surface. LEED spots from this surface characterize the surface as an incommensurate superstructure, which is commensurate in the [110] direction and incommensurate along the [001] direction of the FeAl(110) surface. STM results detailed the atomic structure of this incommensurate phase, elucidating a quasi-hexagonal arrangement of atoms, shown in Fig. 1(a). The structural model of this phase, determined from the STM image, is depicted in Fig. 1(b). Comparing the STM data and the structural model, the hexagonal mesh drawn with a solid line [Fig. 1(b)] reveals the imaged atoms being Fe, surrounded by six Al atoms, which are not imaged with STM. The model proposed for this structure contains two Al and one Fe atoms, which indicates that this surface corresponds to an FeAl\(_2\) stoichiometry, which is consistent with previous AES and x-ray diffraction results.\(^8-10\)

The ultra-thin aluminum oxide film is formed on this reconstructed surface after exposing 1000 l O\(_2\) at and above 800 °C. The LEED and STM studies show that this is the only temperature range that a well ordered oxide film is produced. Below this range, amorphous and disordered thin films are formed. The disappearance of the incommensurate diffraction spots for saturation coverages (1000 l) indicates that the interfacial layer between the oxide film and substrate does not maintain its reconstructed structure. Figure 2 shows a STM image of a regular and nearly hexagonal pattern of the oxide film. The image was recorded after the sample, with a bias of \(-1.25\) V with the respect to the tip, was recooled to room temperatures. The spot to spot distance is obtained to be 19 Å and the unit cell of the oxide film, shown with a solid line, is measured as 18.6 × 19.4 Å\(^2\). The STM image shows that the oxide film has a flat and homo-
geneous morphology. As obviously seen in Fig. 2, a small lateral disorder exists along the [110] direction. LEED also confirms this disorder with streaking along this direction.

As mentioned, there have been no detailed studies to expose the electronic structure of thin Al₂O₃ on FeAl(110) other than the preliminary XPS studies of Graupner et al.⁵ We have conducted ARPES and XPS measurements and the results are presented here to elucidate the electronic structure of the thin oxide film formed on FeAl(110). The shallow Al-2p core levels measured at a photon energy of 150 eV within the normal emission geometry for the clean and oxidized surfaces are shown in Fig. 3. The peak from the clean surface is centered at 72.5 eV and it is clearly seen that it is attenuated after exposure to a saturation coverage of oxygen. Upon the oxygen exposure, the broad peak that emerges at ~2–3 eV higher binding energies is associated to Al species in the oxide film, consistent with similar systems.³,¹¹ Moreover, the weak shoulder at 73.9 is attributed to Al atoms at the interface layer between the oxide film and the substrate.

The presence of this layer was stated in Al₂O₃/NiAl(110) (Ref. 3) and O₂/Al(111),¹¹ wherein the same peak was observed at the same binding energy obtained here. As seen from Fig. 4, the intensity variation of this peak follows the substrate intensity variation as the emission angle changes from normal to 60° in which the latter angle is more surface sensitive. This confirms the existence of an interfacial layer consisting of a metallic Al.

In order to prove that Al is the only constituent in the thin oxide film, as in the case of NiAl, photoemission spectra of the Fe-3p core level of the clean and oxidized surfaces were collected with a photon energy of 140 eV at normal emission. As shown in Fig. 5, a comparison of the clean and oxidized spectra reveals no chemical shift in the core level of Fe-3p. Figures 3 and 5 conclude that the only species that oxidizes on the surface of FeAl(110) crystal is the Al atoms.

To probe the electronic dimensionality behavior of the thin oxide film, the valence band structure of the oxide film was measured by ARPES using s+p-polarized light, which corresponds to 45° incidence angle of the photon beam with respect to the substrate normal. The sample was rotated to acquire the band dispersion in the plane of the surface as a

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FIG. 2. STM image (70×70 nm², Vᵣ=−1.25 V, and Iᵣ=−0.7 nA) of the oxidized FeAl(110) surface after exposing to 1000 l of O₂ at 850 °C. The unit mesh of the oxide structure (1.86×1.96 Å²) is shown with a solid line.

FIG. 3. Photoemission spectra of Al-2p peaks for clean and oxidized surface. The spectra were taken at normal emission geometry and 150 eV photon energy.

FIG. 4. Al-2p photoemission spectra of oxidized surface of FeAl(110) taken at normal and 60° emission angle. The attenuated intensity of the weak shoulder (S) at higher emission angle (60°) verifies the existence of an interfacial layer of metallic Al.

FIG. 5. Photoemission spectra of Fe-3p do not show any chemical shift for the clean and oxidized surfaces of FeAl(110).
function of the parallel component of the electron wave vector $k_\parallel$ and the photon energy range of 34–90 eV was used to probe the band structure of the oxide film as a function of the perpendicular component of the electron wave vector. A set of energy distribution curves (EDCs) collected in this geometry for the thin oxide film grown with a saturation coverage of oxygen is shown in Fig. 6. The analyzer and the vector potential are held in the mirror plane along the [110] direction of the substrate for this measurement. The small intensity peaks between 0–5 eV binding energies are due to the photoemission signal from the underlying of the FeAl substrate. The oxygen induced states appear between 5–13 eV. The positions of the three strong emissions from the oxide film are marked with a solid line as a function of photon energies. As clearly seen from the figure, the oxygen derived states in normal emission geometry do not exhibit any significant dispersion as a function of the perpendicular component of the electron wave vector (photon dependence). This dispersionless behavior indicates that these states have little to no coupling in the surface normal direction due to the lack of a long-range transitional order, which is consistent with the limited thickness of the thin film. The peaks at ~4.35 eV for the the spectrum at 38 and 15.85 eV for the EDC of 56 eV are attributed to the emission from Al-2p excited by third and second order monochrometer light, respectively.

With the photoelectron emission along the surface normal ($k_\perp \approx 0$), the lack of dispersion of the valence bands on $k_\perp$ by varying the photon energy implies a two-dimensional electronic structure. Apart from this independence, the necessary condition of the two (one) dimensional electronic structure is the dispersion dependence (lack of dependence) of the valence bands on the parallel component of the electron wave vector ($k_\parallel$) of the surface bands. Therefore, the parallel component of the wave vector was also probed by changing the detection angle at a fixed photon energy. The EDCs in Fig. 7 were taken for a 76 eV photon energy along two high symmetry directions in the surface Brillouin zone of FeAl(110), that is, $\mathbf{A} \perp [001]$ [Fig. 7(a)] and $\mathbf{A} \perp [1\bar{1}0]$ [Fig. 7(b)]. The observed strong band dispersion along both mirror planes indicates a well-defined in-plane band structure. This indicates that, due to the lack of dispersion of bands as a function of the perpendicular electron wave vector, the thin oxide film solely comprises a two dimensional electronic structure. Oxygen derived $p$ states dominate the photoemission spectra. The intensities of valence bands of FeAl substrate are more attenuated at higher emission angles, which imply that the oxide thin film is very homogeneous and wets the underlying substrate. These ARPES results also confirm that Al is the only metal component of FeAl in the oxide film, because if there were any elemental Fe involved in the formation of oxide film the intensities of the states at and near the Fermi level, which fundamentally arise from electronic bands of Fe atoms, would be augmented. Indeed, only attenuated Fe states are observed in photoemission spectra. Moreover, here the attenuated states between 0–5 eV are similar to the clean FeAl photoemission spectra (see Fig. 8), and these features do not resemble the FeO or Fe$_2$O$_3$ electronic structure probed in the previous studies,12,13 We can conclude that the elemental Fe, FeO, and Fe$_2$O$_3$ are not involved in the oxide layers.

The question of whether this unique ultrathin oxide film has a local density of states in the band gap of the bulk oxide has been considerably searched with theoretical studies in the last decade.14 In order to probe and judge this conception,
with experimental results, clean FeAl(110) photoemission spectra are compared with the photoemission spectra of Al₂O₃/FeAl(110) as shown in Fig. 8. Since the FeAl features in the photoemission spectra of the oxide film are attenuated, the intensities of the clean FeAl(110) spectra are normalized to the intensities of the substrate features in the spectra from the oxidized surface. In both geometries (A ⊥ [001] and A ⊥ [110]) the measurements were acquired at 70 eV photon energy and normal emission. The peaks above the Fermi level for the oxide film are due to the emission from the second order light from the TGM. The photoemission spectra of the FeAl and thin oxide film reveal the same features between 0–2 eV binding energies; however, the spectra show different electronic structures between 2–4 eV. An enhanced peak located at 2.97 eV has been noticed for the case of the oxide thin film in both photoemission geometries. The contention that this peak corresponds to the Σ₁ band of the clean FeAl(110) surface can be ruled out, since, in principle, this state would be attenuated in a surface covered with a thin oxide film. However, in the present case this feature does not exhibit an attenuated intensity but rather shows an enhanced intensity compared to the one in the clean surface. One argument to explain the change seen in the photoemission spectra of the oxide film is that this state might actually arise from an Al-sp state or an interfacial (bonding) state located between the thin film of Al₂O₃ and FeAl(110) substrates. As reported in our previous paper, the close proximity of the binding energy of this state to a tunneling voltage where the STM reveals a zigzag-stripe structure of Al ions also supports the statement that this peak is due to the Al-sp state. However, as stated in Ref. 6, the surface could contain O vacancies; therefore, this state can be induced from defects. Similarly, in the case of annealed TiO₂(110) surface, an induced defect state at 1 eV binding energy emerges within the band gap of the bulk oxide. The interpretations proposed here for the present system necessitate further theoretical calculations of the density of states of an ultrathin film alumina with defective and defect-free surfaces to better understand the nature of the state(s) observed in the band structure of the thin oxide film on this particular FeAl(110) crystal.

IV. CONCLUSION

The electronic structure of the thin aluminum oxide film formed on FeAl(110) was studied with ARPES. XPS results revealed the existence of the Al atoms in the interfacial layer between the oxide film and the substrate. XPS results also confirmed that Al is the only constituent of FeAl which is involved in the oxide structure. The oxide valence states do not show dispersion as a function of the perpendicular component of the electron wave vector; however, they show strong dispersion parallel to the surface. These results conclude that this ultrathin alumina film formed on FeAl(110) exhibits a highly two dimensional electronic structure.

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