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Iron oxide thin film growth on Al_2O_3/NiAl(1 1 0)

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Abstract

The electronic structure and the growth morphology of iron oxide thin films were studied by means of Synchrotron Radiation Photoelectron Spectroscopy (SRPES) and Low Energy Electron Diffraction (LEED). A thin well-ordered alumina film on a NiAl(1 1 0) single crystal surface as a template for iron oxide growth was employed. Two different methods of iron oxide film preparation were applied. In the first attempt, iron deposited at room temperature was subsequently annealed in oxygen. Even though a whole layer of iron was oxidized, an expected long-range order was not achieved. The second attempt was to perform reactive deposition. For this reason iron was evaporated in oxygen ambient at elevated substrate temperature. This method turned out to be more efficient. Diffused but clear LEED patterns of six-fold symmetry indicating hexagonal surface atoms arrangement were observed. From the PES measurements, binding energies for Fe2p for grown iron oxide film were established as well as energy distribution curves for the valence band. Growth curves based on Fe3p core-level peak intensities for iron and iron oxide were plotted identifying type of film growth for both deposition methods. Based upon these results we have found evidence for interdiffusion in the interface between alumina and iron oxide at the early stages of growth. Further deposition led to formation of Fe_3O_4(1 1 1) (magnetite) overlayer. Moreover, the quality of the film could also be improved by long-time annealing at temperatures not exceeding 575 K. Higher annealing temperature caused disappearance of LEED pattern indicating loss of long-range ordering.

Keywords: Molecular beam epitaxy; Thin films; Iron; Iron oxide; NiAl(1 1 0); Reactive deposition; Oxidation; Photoelectron spectroscopy

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1. Introduction

Studying the thin film metal oxide on metal oxide interfaces is significant due to possibility of controlled modification of electrical material properties [1] which are of great importance in application for catalysis [2] or gas sensors [3]. It refers especially when an epitaxially grown overlayer can be stabilized in one of many structural phases as in case of iron oxides. The most stable iron oxide phases are magnetite Fe_3O_4 and hematite α-Fe_2O_3 but there are also metastable maghemite γ-Fe_2O_3 and wustite $Fe_{1-x}O$ (x stands for vacancy formation at the iron sublattice). The oxygen sublattice mismatch between the substrate and the grown film plays a crucial role in epitaxial growth mode as well as in determining the structural phase of the film. Therefore it is rare to achieve heteroepitaxy in case of oxide on oxide growth. From previous studies, α-Al_2O_3 and MgO are well known oxide substrates as a support for iron oxide growth [4,5]. In both cases, insulating properties of the substrates make it rather problematic for a study with electron spectroscopy methods because of charging problems. Therefore it was desirable to create a geometrically and electronically well-defined thin alumina film on top of a metallic substrate. From the literature [6–15] it is well known that oxidation of the NiAl(1 1 0) surface leads to the formation of a well-ordered 5 Å thick alumina layer. The fabrication of alumina on NiAl(1 1 0) has been widely used for support of different metal clusters [16–22] The relatively easy way of alumina layer fabrication and high reproducibility make

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NiAl(1 1 0) substrate an interesting solution for iron oxide film growth.

We have found conditions for fabricating an epitaxial $FeO_x/Al_2O_3(0001)/NiAl(110)$ system. As it will be shown further, we have clear evidence of strong interdiffusion on the interface during the growth followed by a subsequent structural ordering and final $Fe_3O_4(111)$ growth.

2. Experimental

The experiments were carried out in an ultrahigh vacuum system (UHV) at the beam line 5 of the ISA storage ring facility in Aarhus, Denmark, operated with bending magnets. The Zeiss SX700 plane grating monochromator was used to give desired photon energy. Synchrotron radiation photoemission spectroscopy (SRPES) data were obtained from a VG CLAM spectrometer running at 30 eV pass energy. The UHV chamber was equipped with standard surface science tools such as a noble gas sputter gun, low-energy electron diffraction (LEED) optics, a mass spectrometer, a gas inlet system and an evaporator sources for metal and oxides evaporation. The base pressure during measurements was 5×10^{-8} Pa. As it was mentioned before, we have used a NiAl single crystal with polished and well oriented (1 1 0) surface as a template for alumina film growth. The NiAl substrate was cleaned in UHV by repeated cycles of sputtering with 3 keV Ar^+ ions and annealing up to 1100 K. These cleaning cycles were repeated until LEED and SRPES indicated well-ordered and clean (carbon free) surface. The alumina thin film preparation procedure as described in details by Jaeger et al. [6] consists of 15 min oxidation at $p = 1.2 \times 10^{-4}$ Pa of O_2 at $T = 550$ K followed by subsequent annealing at $T = 1100$ K for 5 min. The oxygen was introduced through a nozzle placed a few millimeters from the sample surface. In this way, O_2 was locally dosed preventing it from contaminating the whole system with high pressure of oxygen. Three to five cycles were enough to fabricate a uniform 5 Å thick layer of Al_2O_3. The quality and film composition are checked by LEED and PES. Iron film was deposited using a MDC e-Vap 100 source filled with a high purity (99.99%) iron rod. The film thickness was monitored during the growth by quartz crystal microbalance and the typical growth rate was 5 Å/min. All photoelectron spectra were recorded at room temperature.

All core-level spectra were fitted using pseudo-Voigt (Lorentzian convoluted with Gaussian) peak-shape and Shirley type of background. All fitting parameters were kept free during iteration and only some of them, as it will be discussed letter, were kept within narrow energy limits. The energy range for all spectra was calibrated against the Fermi level (E_F) of NiAl(1 1 0).

3. Results and discussion

3.1. Preparation of Al_2O_3 thin film on NiAl(1 1 0)

Before oxidation, a sharp rectangular LEED pattern (Fig. 1a) of the NiAl(1 1 0) surface was seen ($a = 2.89$ Å, $b = 4.08$ Å, $\alpha = 90°$). After 3 cycles of oxidation and annealing, the LEED pattern (Fig. 1b) indicated two domain formations of a much larger unit-cell ($a = 10.6$ Å, $b = 17.9$ Å, $\alpha = 88.7°$). According to previous investigations the phase of 24.1° rotated domains is close to γ-alumina [7–13] or the κ-alumina structure with slightly extended lattice constants [14]. Most recent research points rather to a completely new structure not related to any of the bulk corundum phases [15]. Intensity and sharpness of the LEED pattern imply that we are dealing with a well-defined, long-range ordered structure of the $Al_2O_3(0001)$ surface.

SRPES of the Al2p levels was applied to investigate the oxidation level. The spectra are not introducing anything new into the subject, thus there is no reason to display them in this paper. The Al2p exhibits the doublet due to degeneration because of spin-orbit splitting. The intensity ratio between $Al2p_{1/2}$ and $Al2p_{3/2}$ components is 1:2, splitting about 0.4 eV and the positions are 72.2 eV and 72.6 eV, respectively, for the metallic aluminum. After oxidation, the metallic components of Al2p state were still observed although the intensity of the components around 74 eV was an order of magnitude larger. The shift to the higher binding energies (BE) should be expected for the species in the oxidized state. Even though the spectra after oxida-

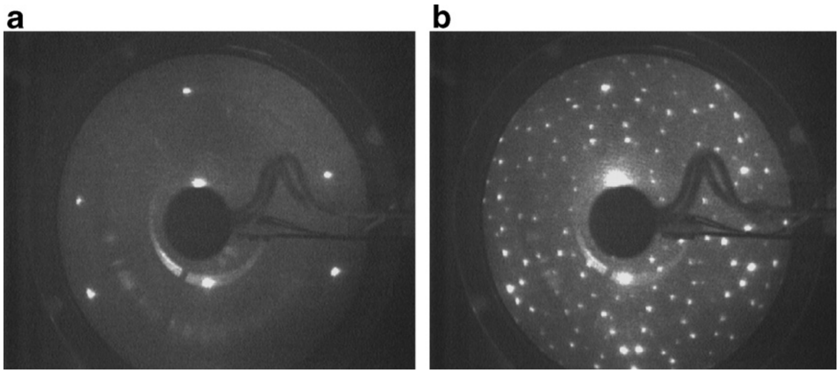

Fig. 1. LEED patterns of the NiAl(1 1 0) surface (a) and after cycles of oxidation and annealing (b). Both images recorded at 86.4 eV.