Topic area: **CMMSP**

Investigation of Misfit Dislocations at the Fe_2O_3/Al_2O_3 interface

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Abstract
Recent studies of buried interface α-$Fe_2O_3(0001)/\alpha$-$Al_2O_3(0001)$ using high resolution transmission electron microscopy (HRTEM) and ion scattering techniques reveal the existence of disordering at the interface due to the misfit dislocations. Molecular dynamics (MD) calculations were carried out to understand the formation of misfit dislocations and the interface structural features. The misfit dislocations are formed because of the lattice mismatch between the substrate and the film. Ion scattering simulations were carried out using VEGAS code, in which the atomic positions generated by the MD calculations were used. The hitting probabilities determined from these simulations were compared with the experimental surface and interface peaks obtained from the aligned RBS spectrum.

Introduction
The wide range of physical properties exhibited by oxides suggests that oxide chemistry will be richer than those of metals. The growth of iron oxide thin films with good crystalline quality is of increasing interest due to their importance in heterogeneous catalysis, magnetic thin films, surface geochemistry, corrosion, and integrated microwave devices [1]. Recently, several high-quality well-oriented single crystal iron oxide films with various stoichiometries have been synthesized using the molecular beam epitaxial (MBE) growth method and the structural properties have been analyzed by various surface and bulk sensitive techniques [2, 3].

The physical and chemical properties of interfaces play major roles in the growth of high-quality thin films. For the most cases, the interface between the film and the substrate initiates the defects in a thin film. Thus, defects and their spatial distribution within a film may be controlled by carefully tailoring the factors which control the interface structure. In general, the factors which determine the interface structure between a film and a substrate include the in-plane lattice mismatch, termination species of the surface and surface relaxation state of the substrate, crystallographic orientation relationship between the film and the substrate, phase compatibility between the film and the substrate, and deposition temperature. In the case of iron oxide thin films grown on Al_2O_3 substrates, disorder at the interface of hematite films and sapphire substrates, was previously reported [4, 5]. It was suspected that the disordering at the interface was due to misfit dislocations at the interface.

High-energy ion scattering technique such as Rutherford backscattering spectrometry (RBS) along with channelling has been widely used to characterize buried interfaces and crystalline quality of thin films. In this study, RBS along the channelling and random geometries was used to investigate the disordering at the interface. In addition, high-resolution transmission electron microscopy (HRTEM) was used to map the misfit dislocations at the interface. Molecular dynamics (MD) calculations were carried out to understand the formation of misfit dislocations and the interface structural features of this system. Atomic positions generated by the MD calculations were used in the ion scattering simulations and the hitting probabilities

were determined. They were compared with experimental surface and interface peak areas obtained from the aligned RBS spectrum.

Experimental

The samples were grown in the molecular beam epitaxial (MBE) facility at the Environmental Molecular Sciences Laboratory (EMSL) at PNNL. The high-energy ion scattering experiments were carried out in the accelerator facility at the EMSL, which is described in detail elsewhere [6]. The surface orientation was (0001) and the standard dose of helium ions for one spectrum was 6.2×10^{15} ions/cm^2. The backscattering spectra were collected using a silicon surface barrier detector at a scattering angle of 150°. For the 70 nm specimen, one cross-sectional thin foil was prepared such that the HRTEM images can be taken from the zone axis $[01\bar{1}0]$. HRTEM analysis was carried out on a Jeol JEM 2010 microscope with a routine point to point resolution of 0.194 nm. Modelling of interface misfit dislocations was carried out using molecular dynamics (MD) calculations. The atomic positions generated by the MD calculations are used in the ion scattering simulations. Ion scattering simulations were carried out using VEGAS code, which uses Monte Carlo calculations and a Moliere screened potential and it is described elsewhere [7]. Monte Carlo method is used to determine the ion trajectories inside the crystal. Once the projectile ion has a close encounter with an atom in the crystal cluster, the probability that the ion hits this atom (hitting probability) is evaluated. A deflection angle is calculated and the resulting new direction of motion of the ion is obtained and the next possible atom for collision will be selected. This procedure will be followed until the ion leaves the crystal. The sum of the hitting probabilities of the atoms in one row (atoms/row) depends on thermal vibration of atoms and the width of the shadow cone.

Results and Discussion

Aligned and random RBS spectra for the 70 nm film are shown in Fig. 1. There are five peaks visible in the aligned spectrum. The first peak at the high-energy side is the Fe surface peak at the front of the film. The second peak is attributed to some Fe atoms visible to the ion beam at the interface (back surface of the film). Apparently the ion beam sees some A*l* atoms (substrate surface) at the interface as indicated by the third peak. The fourth peak is related to the backscattered ion contribution due to the surface oxygen atoms of the film and the fifth peak is due to the visibility of oxygen to the ion beam at the interface.

Because the Fe and A*l* atoms are visible to ion beam at the interface, there must be some disordering of the iron oxide film at the interface or there must be substrate-film mixing present at the interface. Although mixing of the substrate and the film is possible at the interface, no evidence for mixing has been observed in the random spectrum within the experimental resolution and the uncertainties. It could be that the lattice mismatch between the substrate and the film is too large (5.4%) to allow a continuous channelling trajectory through the interface between the two crystal structures.

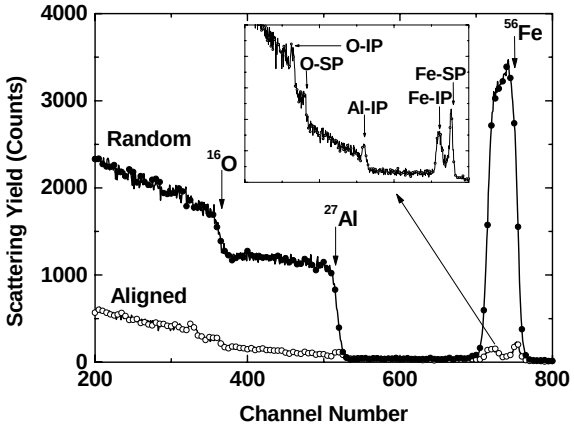

Figure 1: Aligned and random RBS spectra from epitaxially grown 70 nm thick α-Fe_2O_3 (0001) film on α-A*l*$_2O_3$ (0001) substrate. Incident energy of the He^+ was 2.04 MeV and the scattering was 150^o. Magnified version of the aligned spectrum is presented in the insert.

As a result of this lattice mismatch, misfit dislocations were observed in the HRTEM micrographs. Detailed investigations of microstructures along different low index axes were reported previously [5]. In this paper, we present the high-resolution transmission electron microscopy analysis along $[01\bar{1}0]$ axis in Fig 2 (a). There are three dislocations in this region. The dislocation core is characterized by an extra $(\bar{2}110)$ plane on the α-Al_2O_3 side of the interface. This extra half plane terminates at the interface and there is no standoff for this misfit dislocation. It appears that the lattice mismatch between the film and the substrate is relaxed primarily through the formation of interface misfit dislocations.

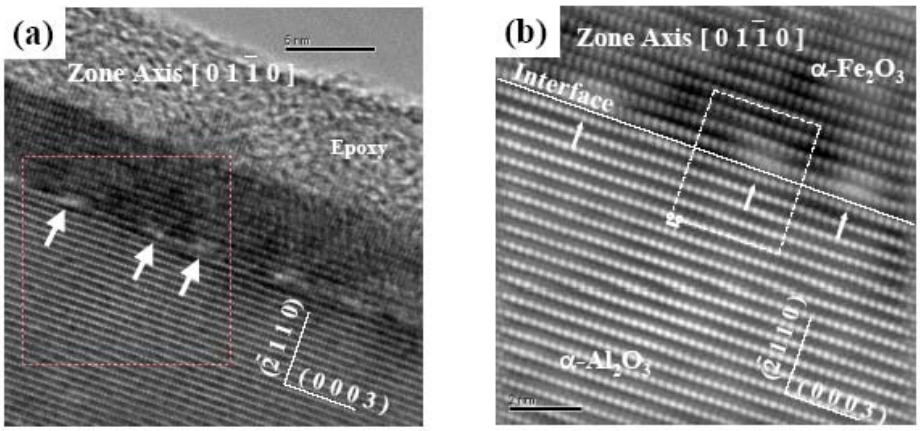

Figure 2: (a) HRTEM micrograph of the interface misfit dislocations imaged from the $[01\bar{1}0]$ zone axis in which three misfit dislocations are present in the box marked by dashed lines. (b) The magnified and Fourier filtered image of the region in (a) showing an extra lattice plane in the α-Al_2O_3 side as indicated by the white arrow.

Details of MD calculations performed to simulate the formation of misfit dislocations at the Fe_2O_3/Al_2O_3 interface are described elsewhere [8]. Initial interface structure and the structure after relaxation along the $[1\bar{1}00]$ direction are shown in Figs. 3 (a) and (b), respectively. Light and dark spheres illustrate iron and aluminium atoms in the film and substrate, respectively. The oxygen atoms were removed from these figures for easy visualization. After relaxation, two misfit dislocations can be clearly seen, and the dislocation cores area defined by $(01\bar{1}2)$ and $(01\bar{1}4)$ extra planes in the Al_2O_3 substrate. These planes terminate at the interface, as seen in the HRTEM images.

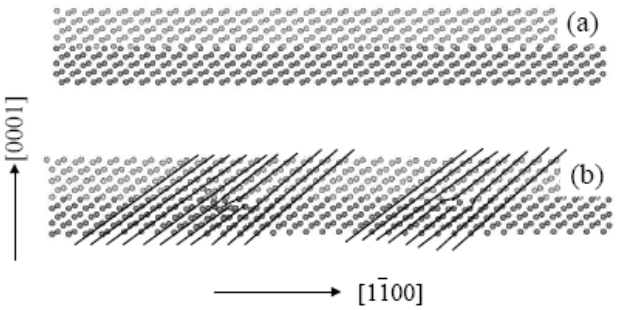

Figure 3: Atomic plots showing (a) the initial configuration of the interface along $[1\bar{1}00]$ direction, when viewed from $[11\bar{2}0]$ direction, and (b) the final configuration after relaxation. The solid lines are sketched to reveal extra lattice planes in the α-Al_2O_3 side.

The VEGAS [7] simulation program has been used to calculate the hitting probability of the atoms in the surface and interface regions. These hitting probabilities can be correlated with the area of the peaks that appear on the experimental channelling spectrum (Fig. 1). The relaxed supercell of the MD calculations contains four misfit dislocations, two of them are near the

fixed boundary and the other two are in the middle. The two misfit dislocations at both edges were discarded and a large cluster around the other two misfit dislocations in the middle was used in the VEGAS calculations. Because the size of the cluster is large, it has been divided into several small clusters for the VEGAS calculations. These clusters were used with appropriate boundary conditions in VEGAS calculations to determine the hitting probabilities of an incident ion in terms of atoms/row due to Fe atoms at the surface and interface and A*l* atoms at the substrate. Results of these simulations along with the experimental areas of surface and interface peaks are summarised in Table 1. An excellent agreement was found between simulated and experimental surface and interface peaks except in the interface peak corresponding to A*l*.

Table 1: Summary of experimental (from the aligned RBS measurements) and theoretical (from ion scattering simulations) values surface and interface peaks areas.

Peak Description	*Experimental Peak area (atoms/row)	**Hitting Probability (atoms/row)
Fe – Surface Peak	3.9 ± 0.1	4.0
Fe – Interface	4.3 ± 0.1	4.3
A*l* – Interface	7.3 ± 0.2	8.7
A*l* – Surface Peak (substrate alone)	6.2 ± 0.2	6.1

* from the aligned a RBS Spectrum of epitaxially grown 70 nm thick α-Fe_2O_3 film on α-Al_2O_3 substrate

** From the simulations of 10 nm thick α-Fe_2O_3 film on α- Al_2O_3 substrate

Conclusion

Ion scattering techniques along with HRTEM studies of the buried interface of epitaxially-grown α-$Fe_2O_3(0001)/\alpha$-$Al_2O_3(0001)$ show the occurrence of disordering at the interface due to the misfit dislocations. The formation of misfit dislocations and the interface structural features has been studied using molecular dynamics. Atomic positions generated by the MD calculations were used in the ion scattering simulations and hitting probabilities of the atoms in the surface and interface regions were determined. Results from these simulations were compared with the experimental surface and interface peaks obtained from the aligned RBS spectrum and found to be in excellent agreement.

Acknowledgements

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