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The oxidation of Fe(111)

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ABSTRACT

The oxidation of Fe(111) was studied using Auger electron spectroscopy (AES), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS) and scanning tunnelling microscopy (STM). Oxidation of the crystal was found to be a very fast process, even at 200 K, and the Auger O signal saturation level is reached within ~50×10^{-6} mbar s. Annealing the oxidised surface at 773 K causes a significant decline in apparent surface oxygen concentration and produces a clear (6×6) LEED pattern, whereas after oxidation at ambient temperature no pattern was observed. STM results indicate that the oxygen signal was reduced due to the nucleation of large, but sparsely distributed oxide islands, leaving mainly the smooth (6×6) structure between the islands. The reactivity of the (6×6) layer towards methanol was investigated using temperature programmed desorption (TPD), which showed mainly decomposition to CO and CO_2, due to the production of formate intermediates on the surface. Interestingly, this removes the (6×6) structure by reduction, but it can be reformed from the sink of oxygen present in the large oxide islands simply by annealing at 773 K for a few minutes. The (6×6) appears to be a relatively stable, pseudo-oxide phase, that may be useful as a model oxide surface.

1. Introduction

The interaction of oxygen with iron is of great interest in a wide range of technological areas including corrosion, metallurgy, data recording media and construction and research in the area has a long history. As a result, the majority of studies in the literature concerns the oxidation of iron sheet in ambient conditions and there is relatively little work using pure oxygen and well-defined surfaces, particularly the (111) plane, which, because of its open structure, is likely to be the most reactive of the low index surfaces. Studies of oxygen adsorption and oxide growth on Fe(110) and (100) surfaces have been reported using STM [1–3], LEED/AES [2,4–7], and XPS [8–10] and although it is generally agreed that oxide formation follows oxygen chemisorption, there remains some debate over the kinetics, mechanism and structures evolving at the earliest stages of oxidation.

A study by Qin et al. described AES, LEED and STM results on the oxidation of Fe(111) at 300 and 500 K. At 300 K there was a rapid initial uptake of oxygen, with saturation of the Auger signal achieved after around 200 L exposure, whilst at 500 K oxygen uptake is directly proportional to exposure and no saturation is observed in the O/Fe peak ratio up to 4200 L [1]. In addition, they report the formation of different oxide phases at the two different temperatures, with both Fe_3O_4 and Fe_2O_3 forming at 300 K but predominantly Fe_3O_4 at 500 K. STM images showed that after oxidation at 300 K, the surface was uniformly covered in small (5 to 15 nm wide) oxide islands, whereas oxidation at 500 K resulted in significantly larger islands (100 to 300 nm wide) with patches of bare substrate in between.

Formation of oxide islands after room temperature oxidation of Fe(111) was previously reported in an STM and AES study which also reported dewetting of the islands from the surface after annealing, resulting in the appearance of larger oxide islands separated by regions of Fe accompanied by a decrease in the Auger O/Fe peak ratio [2].

An XPS study of the oxidation of polycrystalline iron found that the oxide films produced contained a mixture of Fe_3O_4 and γ-Fe_2O_3 with no distinct boundaries between them [10]. Other groups have also reported mixtures of oxide states at the surface after oxidation of iron [11–14].

The aforementioned work [10] proposed an oxidation mechanism in which oxygen adsorption is followed by thin layer oxide formation via place exchange which terminates after a few monolayers. Subsequently, electron tunnelling from the metal towards the oxygen produces an electric field which induces outward cation diffusion leading to Fe_3O_4 growth, whilst inward anion diffusion produces γ-Fe_2O_3 growth. There is some debate within the literature with regards to which mechanistic step is rate-determining. Grosvenor et al. have measured activation energies for Fe oxidation by both O_2 and water vapour and found the values to be the same despite the fact that oxidation by O_2 resulted in the formation of thicker oxide layers. From this they concluded that place exchange is the rate determining step [15]. Other groups are of the opinion that the electric field driven ionic diffusion is rate determining since the reaction between the metal and oxygen takes place at the oxide/oxygen interface and therefore the metal cations must diffuse through the oxide layer for the reaction to continue [16–18].

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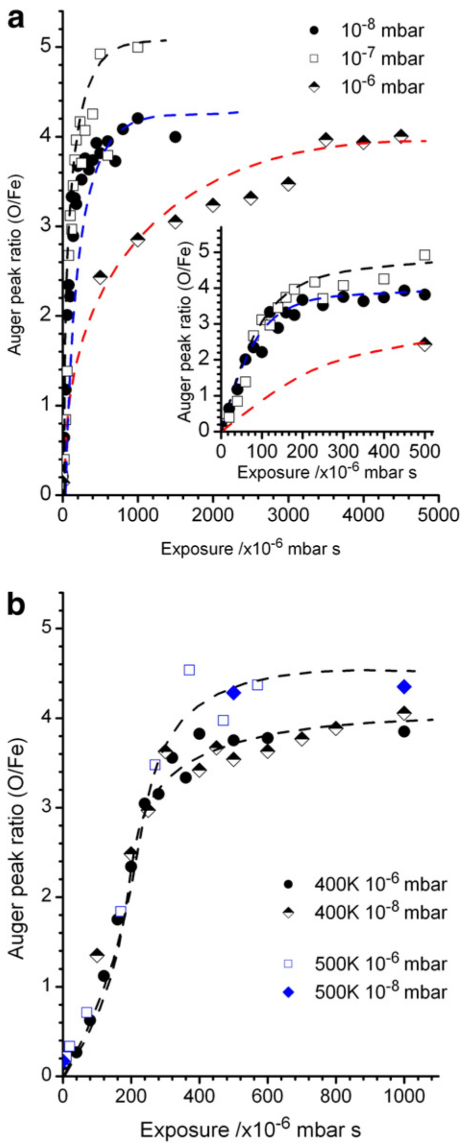

Fig. 1. a.) Auger uptake curves for adsorption at 298 K. b.) Auger uptake curves for adsorption at 400 K and 500 K.

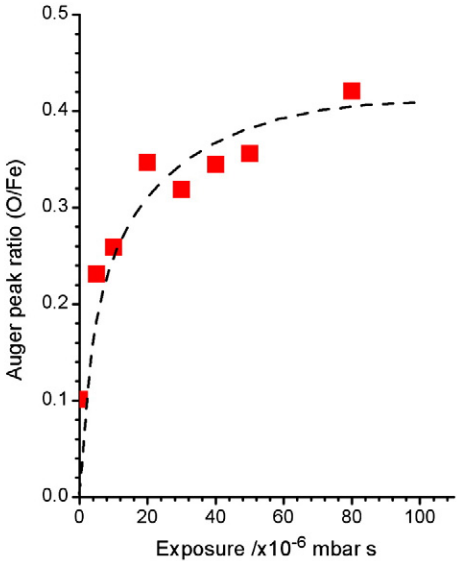

Fig. 2. Auger uptake curve for adsorption at 773 K. The exposure is only shown up to 80×10^{-6} mbar s to emphasise the shape of the curve at low exposures, but the Auger signal has already saturated — higher exposures up to 500×10^{-6} mbar s give a ratio of 0.4(±0.05).

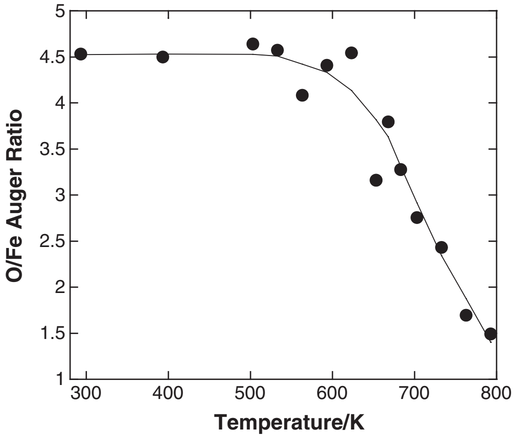

Fig. 3. The effect of annealing temperature, after oxygen adsorption at 298 K for 1000×10^{-6} mbar s, on the Auger signal ratio (measured after cooling).

The aim of the current work was to use a wide range of complementary surface sensitive techniques to explore the rate of oxidation and structures formed during the oxidation of Fe(111) in more detail.

2. Experimental

The experiments were carried out on three pieces of equipment: a small ultra high vacuum (UHV) system for TPD and LEED/Auger measurements (UHV I), a custom-designed Omicron Multiprobe UHV system (UHV II), and a system equipped with XPS and a thermal molecular beam system (UHV III). UHV I comprises of a stainless steel chamber maintaining a base pressure of ~5×10^{-10} mbar equipped with a PSP ISIS ion gun for sample cleaning, an OCI system for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a Hiden quadrupole mass spectrometer for TPD measurements. The Fe(111) crystal was mounted on a holder which was attached directly onto the system manipulator. W wires were spot welded onto the underside of the sample holder to achieve direct heating. The temperature was recorded through a thermocouple inserted into a small hole in the side of the crystal. For TPD experiments and annealing, methanol and oxygen were dosed via a leak valve through a stainless steel dosing tube, directed at the sample. The methanol source (Fisher, 99.8%) was cleaned by repeated freeze–pump–thaw cycles.

UHV II consists of four UHV chambers pumped by three turbo pumps and four ion pumps, giving typical base pressures of ~1×10^{-9} mbar.

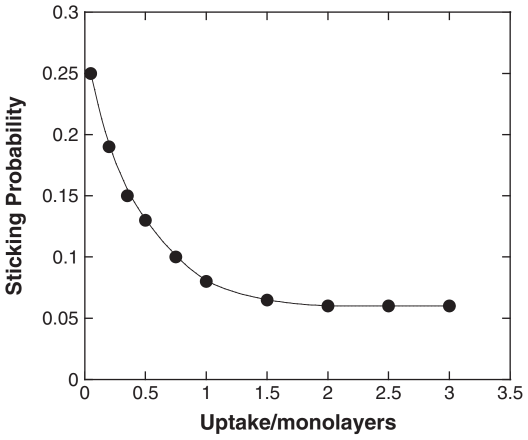

Fig. 4. Sticking probability dependence on oxygen uptake at 290 K.