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ToF-SIMS studies of the oxidation of Fe by D_2O vapour: comparison with XPS

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The oxidation of iron (Fe) by water (D_2O) vapour at low pressures and room temperature was investigated using time-of-flight (ToF) SIMS. The results supported those found previously using XPS and the QUASES™ program in that a duplex oxide structure was found containing a thin outer surface hydroxide ($Fe(OD)_2$) layer over an inner oxide (FeO) layer. The extraordinary depth resolution of the ToF-SIMS profiles assisted in identifying the two phases; this resolution was achieved by compensation for surface roughness. A substantial concentration of deuterium was found in the subsurface oxide layer. This observation confirmed previous assessments that the formation of FeO was from the reaction of $Fe(OD)_2$ with outward-diffusing Fe, leaving deuterium as a reaction product. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: ToF-SIMS; XPS; Fe, oxidation; QUASES™

INTRODUCTION

Previous research performed in this laboratory on the oxidation of Fe by water vapour using XPS and a spectral modelling program called QUASES™ indicated that the oxide layer formed at low pressure (10^{-2}–1 Pa) and room temperature consisted of a layer of $Fe(OH)_2$ over FeO.[1] The formation of subsurface FeO was suggested to occur by the reaction of $Fe(OH)_2$ with outward-diffusing cationic Fe and the formation of surface hydrogen.[1] The thickness of the oxide layer was found to be much thinner than that formed when oxygen gas was used for comparable exposures.[1] The lower oxide thickness formed is water vapour rather than O_2 could be explained by: the presence of hydrogen within the oxide, restricting ion diffusion;[1,2] or the presence of adsorbed hydrogen, causing a reduction in the number of surface sites available for H_2O adsorption;[1,3,4] or the slow rate of conversion of hydroxide to oxide (ie. $Fe(OH)_2$ to FeO).[1]

Without being able to determine directly the hydrogen content within the film, it is difficult to determine if the above reasons are reasonable explanations for the lower oxide thicknesses formed in H_2O vapour compared with O_2. For this reason, time-of-flight (ToF) SIMS was used to examine the oxidation of Fe by D_2O vapour, with the results being compared directly to those determined previously by XPS. Deuterium oxide rather than H_2O was used because hydrogen is a common background contaminant in all vacuum systems. In addition to the question of H (D) involvement in oxide film growth, the highly resolved ToF-SIMS profiles also allow for an assessment to be made of the accuracy of the models developed using XPS and QUASES™.

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EXPERIMENTAL

Pure (99.995%) polycrystalline Fe from Alfa Aesar was polished down to 0.05 γ-Al_2O_3 to produce a mirror finish and placed into an Ion-ToF(GmbH) ToF-SIMS IV single-reflectron mass spectrometer. The surface was sputtered for 30 min using a 3 kV Ar^+ beam (with a 140 nA target current) to produce a contaminant-free surface. After cleaning and without removal from the instrument, the surface was exposed at room temperature to pure D_2O vapour in the introduction chamber at a pressure of $(2–5) \times 10^{-2}$ Pa for 2000 s and again for 200 s after being cleaned for a second time. Any dissolved gases present in the D_2O liquid were removed by multiple freeze–pump–thaw cycles. After dosing was complete, the newly formed surface oxide was depth profiled by monitoring the negative secondary ions produced by a 3 kV Cs^+ sputter beam (10 nA target current) and a pulsed 25 kV $^{69}Ga^+$ analysis beam (2.5 pA target current). The sputter crater was 500×500 μm and the crater produced by the gallium analysis beam (centred within the sputter crater to avoid edge effects) was 200×200 μm in size. The interlaced dual-beam profiling mode was used, along with a two-scan sum per data point. The depth profile was acquired until just after the oxide/metal interface was breached.

The results were analysed using the IONSPEC[5] and IONIMAGE[6] suite of programs. Owing to a small amount of surface roughness created on the surfaces by the Ar^+ sputter

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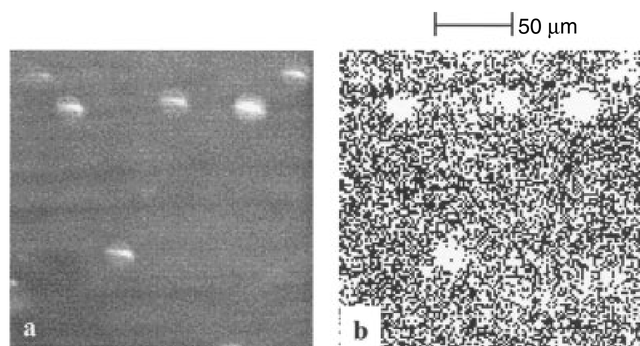

Figure 1. (a) Total negative ion image of the entire depth profile from the surface oxidized by D_2O vapour for 2000 s. The white regions show areas of greater topography then the rest of the surface region analysed. (b) Raster image taken at the oxide/metal interface upon completion of the Cs^+ ion beam depth profile, showing the area (black pixels) used to reconstruct the depth profile (45% of the total area). The white areas of this image represent areas containing a different topography (higher) than the black areas. The Ar^+ sputter beam used during cleaning was the cause of the surface topography.

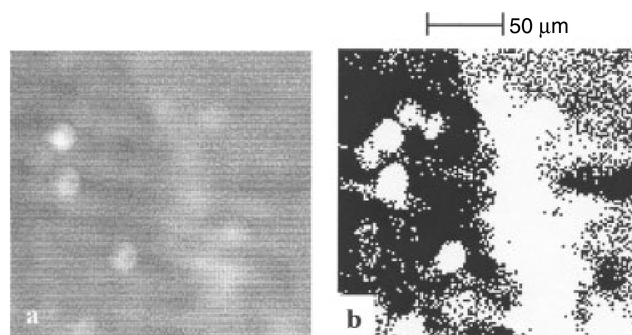

Figure 2. (a) Total negative ion image of the entire depth profile from the surface oxidized by D_2O vapour for 200 s. The white regions show areas of greater topography then the rest of the surface region analysed. (b) Raster image taken at the oxide/metal interface upon completion of the Cs^+ ion beam depth profile, showing the area (black pixels) used to reconstruct the depth profile (50% of the total area). The white areas of this image represent areas containing a different topography (higher) than the black areas. The Ar^+ sputter beam used during cleaning was the cause of the surface topography.

beam, the resulting total negative ion image of the depth profiles from the two oxidation experiments showed areas with differing topography (white areas) compared with the rest of the surface. To correct for this influence on the depth resolution of the profile, the analysis area from each surface was chosen so that only the oxide formed on flat surfaces was analysed. In Fig. 1 the total negative ion image from the complete depth profile of the 2000 s exposure is shown, along with those areas chosen to reconstruct the depth profile. In this way, the depth resolution was improved considerably. The total negative ion image, along with an image showing the areas used to reconstruct the depth profile for the surface exposed to D_2O vapour for 200 s, is shown in Fig. 2.

RESULTS AND DISCUSSION

Figure 3(a) shows the resultant depth profile for the Fe surface exposed to D_2O vapour for 2000 s at room temperature. Emphasis has been placed on signals from the D^-, $^{16}O^-$, FeD^-, FeO^-, $FeOD^-$, $FeOO^-$, $FeOOD^-$ and Fe_2^- ions. The oxide/metal interface is determined to occur at the

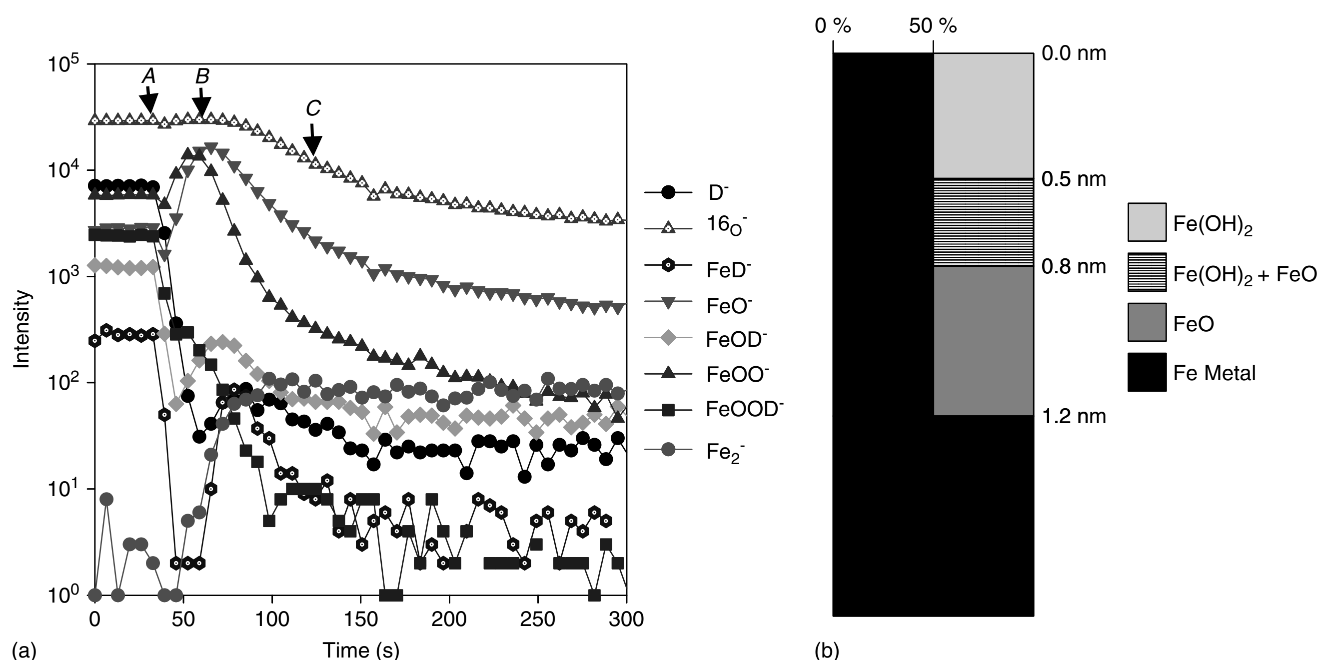

Figure 3. (a) The ToF-SIMS depth profile of Fe surface exposed to D_2O vapour for 2000 s at room temperature. Point *A* found above the $^{16}O^-$ signal represents the interface between the outer $Fe(OD)_2$ layer and the inner FeO layer, whereas point *B* represents the mid-point of the FeO layer. Point *C* represents the point at which the oxide was breached by the Cs^+ sputter beam. (b) An XPS model of the film formed by reaction of Fe with H_2O vapour for 2000 s at room temperature.[1].

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inflection point in the $^{16}O^-$ signal: point *C* in Fig. 3(a). The XPS-QUASES™ measurements previously had determined the oxide thickness to be 1.2 nm after such an exposure.[1] This thickness relates to a layer containing approximately three monolayers of oxide on the metal surface, taking into account the measured thicknesses of single layers of $Fe(OH)_2$ (0.5 nm)[7] and FeO (0.3 nm).[7] The model of the oxide layer determined using XPS and QUASES™ is shown in Fig. 3(b).

Further examination of Fig. 3(a) shows an outer surface region wherein intensities for a number of negative secondary ions remain constant up to point *A*, after which there are sharp decreases in most of the signals. Based upon the strong signals from ions such $FeOOD^-$ and D^-, as well as the earlier XPS-based QUASES™ results[1] (see Fig. 3(b)), this region is identified as containing a near-monolayer of $Fe(OD)_2$. The major drop in these signals at point *A* would suggest that this phase is not as intermixed with the underlying phase(s) as was suggested in the QUASES™ profile (Fig. 3(b)). Some of the negative ions produced in the outermost phase, however, undergo an increase in intensity past point *A*: ions such as FeO^- and $FeOO^-$ are seen to increase in intensity by factors of 5–10, reaching their maximum signal strength at point *B*. Again, based on the earlier QUASES™ result, the underlying phase is interpreted as containing primarily FeO.[1] These results compare well with those found by Tjong and Yeager for similar experiments using ToF-SIMS.[8]

Inspection of the FeD^- and $FeOD^-$ signals shows that these reach a second local maximum at the centre of the FeO phase (point *B* in Fig. 3(a)), thus indicating a separate origin of deuterium in the oxide film besides that found in the $Fe(OD)_2$ surface layer. This is taken as evidence that some deuterium has diffused inward. This could have occurred either during the original chemisorption and decomposition of D_2O on the outer surface[9,10] or during the transformation of $Fe(OD)_2$ to FeO. In any case, it provides evidence of appreciable quantities of deuterium deposited in the subsurface oxide, as was predicted previously.[1] The deuterium found within this layer would most likely reside within defect or interstitial sites.

The presence of any metallic phase can be detected by an increase in the metal dimer ions.[11] In the profile shown in Fig. 3(a), the dimer ion (Fe_2^-) signal increases rapidly to a maximum at a depth just greater than *B* and prior to the decrease in the $^{16}O^-$ signal (point *C* in Fig. 3(a)). The QUASES™ analysis of an equivalent film (Fig. 3(b)) also predicted the presence of metallic Fe intermixed with the oxide. The SIMS profile, however, suggests that the extent of intermixing of metal and oxide is overpredicted by the QUASES™ results and that the metallic contribution is actually found only within the FeO phase.

The ToF-SIMS profile for a 200 s exposure to a comparable pressure of D_2O vapour at room temperature is shown in Fig. 4(a). The QUASES™ profile of the oxide layer formed by reaction of Fe with water vapour and similar exposure conditions is shown in Fig. 4(b). The film thickness found by QUASES™ was 0.8 nm, which is ~70% of the thickness found for the 2000 s exposure. For the ToF-SIMS profile (Fig. 4(a)), the inflection point in the $^{16}O^-$ intensity profile was at 80% of the thickness of that for the 2000 s exposure.

Features in the ToF-SIMS profile for the 200 s exposure are qualitatively similar to those in the profile for the 2000 s exposure but there are important quantitative differences. Most importantly, the intensities for the FeD^- and $FeOD^-$ ions in the inner FeO oxide layer were significantly more prominent than they were in the 2000 s profile. Also, the D^- and $FeOOD^-$ ions present in the outer $Fe(OD)_2$-containing layer of the 200 s profile were less prominent than was found for the longer exposure. These results suggest a substantial

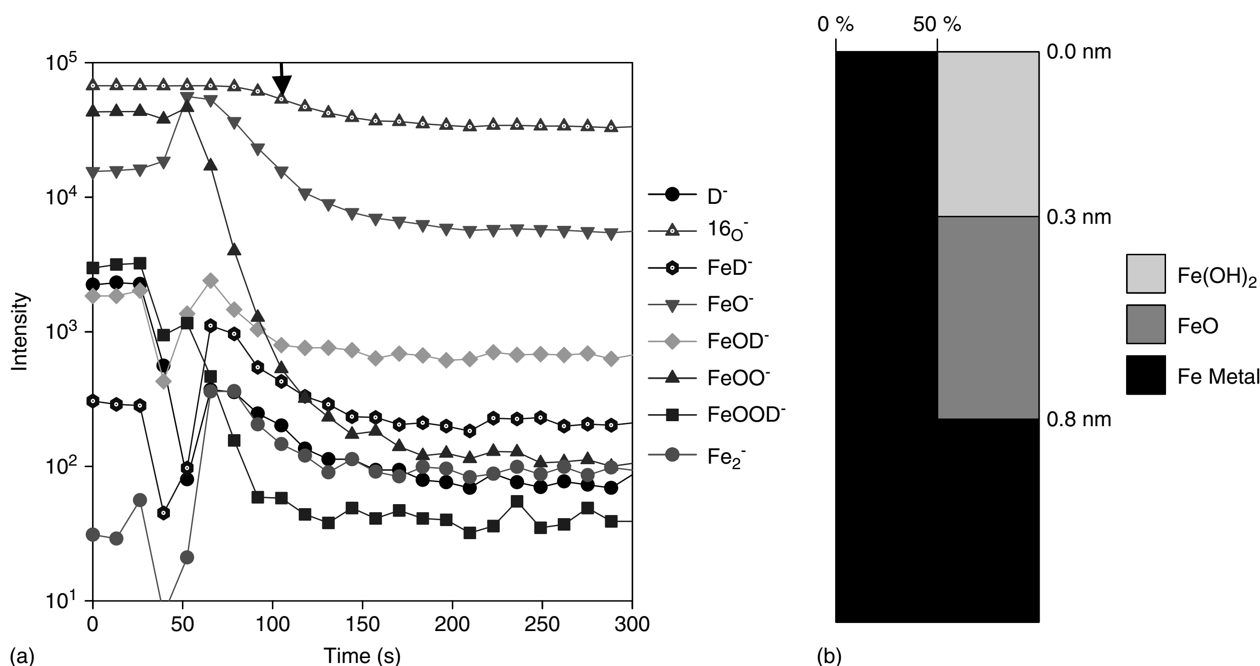

Figure 4. (a) The ToF-SIMS depth profile of Fe surface exposed to D_2O vapour for 200 s at room temperature. The arrow above the $^{16}O^-$ signal represents the point at which the oxide was breached by the Cs^+ sputter beam. (b) An XPS model of the film formed by reaction of Fe with H_2O vapour for 200 s at room temperature.[1].

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mixing of the two oxide species, unlike what was found for the film formed after the Fe surface was exposed to D_2O vapour for 2000 s. Therefore, at this stage in the oxidation a much larger flux of atomic deuterium enters the FeO phase than was found for the film formed after receiving the longer exposure. Some of the deuterium may diffuse into the metal substrate over time, which could account for the lower concentration of deuterium found within the FeO phase of the film formed after receiving a 2000 s exposure compared with the 200 s exposure.

CONCLUSIONS

The ToF-SIMS profiles of these thin oxide films have produced exceptional depth resolution, due partly to corrections for surface roughness. The films analysed compared well with those examined using XPS[1] but with more distinction found between phases at different depths. The presence and location of isotopically labelled hydrogen were directly traceable by ToF-SIMS. Such hydrogen was found not only to be part of the surface $Fe(OD)_2$ layer but also to be distributed within the subsurface FeO layer. This supports previous assessments suggesting that the subsurface oxide layer also contained significant concentrations of hydrogen, which was produced as a reaction product during the conversion of $Fe(OH)_2$ to FeO.[1] This hydrogen may be trapped only temporarily within the FeO layer before diffusing into the metal substrate. From these results it can be stated that the reasons, given in the Introduction, for why the oxide formed by reaction of Fe and water vapour is less than that formed when O_2 is used have not been disproved, but neither was any direct evidence found that undeniably supports these theories.

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REFERENCES

1. Grosvenor AP, Kobe BA, McIntyre NS. *Surf. Sci.* 2004; **572**: 217.
2. Roosendaal SJ, Bakker JPR, Vredenberg AM, Habraken FHPM. *Surf. Sci.* 2001; **494**: 197.
3. Roberts MW, Wood PR. *J. Electron Spectrosc. Relat. Phenom.* 1977; **11**: 431.
4. Maschhoff BL, Armstrong NR. *Langmuir* 1991; **7**: 693.
5. Ion-ToF(GmbH). *IONSPEC*, v. 3.14.9. Ion-ToF: Münster, Germany, 1996–2000.
6. Ion-ToF(GmbH). *IONIMAGE*, v. 2.12.0.15. Ion-ToF: Münster, Germany, 1995–2000.
7. Cornell RM, Schwertmann U. *The Iron Oxides; Structure, Properties, Reactions, Occurrence and Uses*. VCH: New York, 1996.
8. Tjong SC, Yeager E. *J. Electrochem. Soc.* 1981; **128**: 2251.
9. Yu GY, Wallace WE. *J. Solid State Chem.* 1986; **65**: 356.
10. Maieland AJ. In *Recent Advances in Hydride Chemistry*, Peruzzini M, Poli R (eds). Elsevier: New York, 2001; 531.
11. Hultquist G, Seo M, Lu Q, Chuah GK, Tan KL. *App. Surf. Sci.* 1992; **59**: 135.

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