



Surface modification of iron oxides by ion bombardment – Comparing depth profiling by HAXPES and Ar ion sputtering



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ABSTRACT

Thin films of the iron oxide maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) grown on fluorine doped tin oxide (FTO) with pulsed chemical vapour deposition have been investigated with hard X-ray photoelectron spectroscopy. It is found that even low energy sputtering induces a reduction of the surface layer into FeO. Satellites in the Fe 2p core level spectra are used to determine the oxidation state of iron. Depth profiling with changing photon energy shows that the unsputtered films are homogeneous and that the information obtained from sputtering thus, in this instance, represents sputter damages to the sample.

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1. Introduction

There are sixteen oxides and oxyhydroxides of iron [1], with uses ranging from food colouring (E 172) to catalysts. Iron(III) oxide (Fe_2O_3), especially in its hematite phase ($\alpha\text{-Fe}_2\text{O}_3$), exhibit attractive properties for solar water splitting, with a adequate bandgap around 2 eV combined with a favourable position for the valence band's edge and efficient photon absorption. The material is stable, affordable, abundant, nontoxic and environmentally friendly. Said properties have directed significant research efforts regarding hematite as a component in photoelectrochemical cell [2–4].

X-ray photoelectron spectra (XPS) is a standard technique for quantification of chemical states in a material via the chemical shift of core level photoelectron lines [5,6]. Iron oxides present a challenging system to interpret photoelectron spectra from owing to background [7] and satellite structures [8,9] around the Fe 2p region. As mentioned, there are a number of oxides and oxyhydroxides (16) each having different phases which also complicates spectral interpretation.

In this paper we compare spectra of sputtered and unsputtered surfaces of maghemite and hematite taken with 1487 eV photon energy (*i.e.* Al $K\alpha$). The unsputtered maghemite surface and single

crystals of FeO and $\alpha\text{-Fe}_2\text{O}_3$ are also measured with synchrotron based hard X-ray photoelectron spectroscopy (HAXPES) data for comparison.

A synchrotron X-ray source enable us to tune to desired photon energies. Here this have been utilised to obtain increasingly large information depths in the samples at three photon energies above Al $K\alpha$ – without moving the sample position. Since the binding energy (E_b) for the core level electrons that we study is constant, the kinetic energy (E_k) of the studied electrons increase in step with the photon energy ($\hbar\omega$); the kinetic energy is given by Einstein's relation for the photoelectric effect $E_k = \hbar\omega - E_b - \Phi$, where Φ is the work function of the spectrometer. For sufficiently high kinetic energies the mean free path (λ) of the electrons gets larger with incoming kinetic energy. With the so called universal curve for electron mean free paths in mind, this means kinetic energies above 50 eV [10,11]. By using synchrotron radiation the X-ray energy can be varied and thus the available information depth defined as 3λ , gives rise to 99% of the spectral intensity [6]. The longer mean free path in the HAXPES measurements allows us to discern surface oxyhydrides from the bulk sample, which by contrast was impossible with the Al $K\alpha$ photon energy.

We highlight that relying only on standard XPS and sputtering can lead to erroneous interpretation of film composition. It is known that hydroxides and oxides of iron can be reduced by ion bombardment [8,12,13]; sputter damages in the form of preferential removal of lighter species have been shown to occur in physical vapour deposited tungsten sulphide [14], tin sulphide powder [15],

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and nano composite coatings of Ti-Ni-C [16]. Here we specifically use hard X-ray photoelectron spectroscopy with variable photon energy to assess the composition of an *ex situ* sample consisting of an maghemite film grown on fluorine doped tin oxide (FTO).

2. Experimental section

Polycrystalline maghemite and hematite were grown on FTO substrates by pulsed chemical vapour deposition. As precursors, iron pentacarbonyl and O_2 were used. The only difference between the two depositions were the use of either N_2 or CO as carried gas, resulting in the two different polymorphs hematite and maghemite. The investigated thin films were from the same deposition round but not the exactly same film. Further information of the depositions and the deposition parameters can be found in Ref. [17].

Phase determination of the iron oxide films were performed using Raman spectroscopy. A Renishaw micro Raman system was used with the 532 nm line of an argon ion laser. X-ray diffraction was also used and is discussed with associated reference.

The HAXPES experiments were performed at BESSY II (Helmholtz-Zentrum Berlin), at the KMC-1 dipole magnet beam line [18] – using the high kinetic energy photoelectron spectroscopy end station (HIKE) [19,20]. The beam line is equipped with a Si double crystal monochromator (DCM) [21] where the X-rays are focussed on the sample using a paraboloid glass capillary. The base pressure in the measurement chamber was in the 10^{-9} mbar region throughout the experiment. The photoelectron spectra were recorded using a VG Scienta R4000 electron energy analyser at normal emission (90°). For the HAXPES measurements photon energies of 2005, 3000 and 6015 eV were used. All spectra was calibrated with an Au standard with the Au $4f_{7/2}$ binding energy taken to be 84.00 eV [22]. The sputtered films were measured using a Physical Instruments Quantum 2000 ESCA utilizing monochromatized Al $K\alpha$ radiation at a emission angle of 45° . The sputtering of the samples was done at low energy for 8 minutes using 200 V Ar^+ ions. The sputtering was made in a 4+2+2 min. sequence as to reduce the carbon accumulated on the surface, after having exposed the iron oxide films to air. The C $1s$ and Sn $3d$ core level binding energy

regions (Figs. S1 and S2 in the supporting material) were monitored to ascertain that the sputter sequence did not sputter away the iron oxide. Tin is only present within the substrate and was not observed at the information depth using Al $K\alpha$, neither before nor after the sputtering took place. Thus the iron oxide film covers the substrate entirely and island formation may be excluded. The reference measurements were performed on single crystals of FeO(100) and $Fe_2O_3(0001)$ purchased from MaTeck GmbH.

3. Results and discussion

The Raman measurements shown in Fig. 1 are in good agreement with the shifts expected from maghemite and hematite [23]. The hematite film has all the expected peaks and also one at 660 cm^{-1} . This peak arise from possible dislocations and lack of long range order in the film [24]. The maghemite film shown in Fig. 1 consists of maghemite shifts, reported by Faria et al. [23]. Both films showed just one phase, and did not exhibit any sign from other iron oxide phases, like for instance magnetite (Fe_3O_4) or wüstite (FeO), this also indicates that the laser power used for the measurements was low enough as to not reduce the films. X-ray diffraction was also used for characterisation of the deposited films. From the XRD measurements we see both the substrate and the thin film on top. Due to the small thickness of the iron oxide the strongest peaks derives from the FTO substrate but the iron oxide peaks are as well clearly visible. These measurement can be found in Ref. [17].

The nanostructure of the films can be clearly observed in the scanning electron micrographs shown in Fig. 1(b). There is a difference in grain size comparing hematite and maghemite reflecting different growth conditions (for details see Ref. [17]). Neither iron oxide has crystal parameters that match that of the FTO substrate, this promotes growth of clusters which in turn coalesce into a continuous film. The large surface area obtained is beneficial for the intended photoelectrochemical cell application.

In Fig. 1(c) overview spectra and detail spectra (Fig. 2) taken around the Fe $2p$ and O $1s$ regions are displayed. In Fig. 2 four sets of data are compared in the panels: (a) untreated (unsputtered) and (b) sputtered data of maghemite and hematite (c) reference data from single crystal iron oxides, FeO(111) and $\alpha\text{-Fe}_2O_3(0001)$;

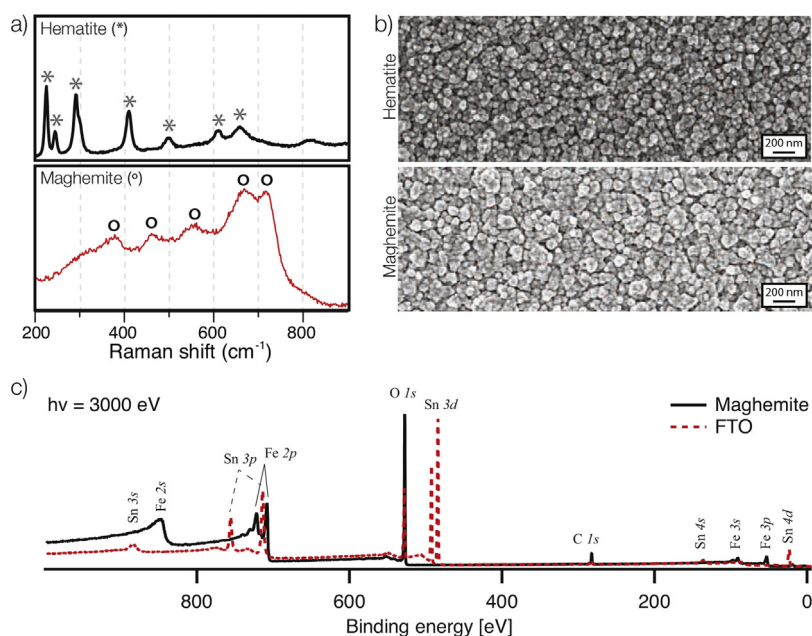


Fig. 1. (a) Raman measurements on the hematite and maghemite films. Panel (b) shows scanning electron micrographs of the nanostructured films. (c) HAXPES measurements of the maghemite film (black) and the FTO used as substrate (dashed).

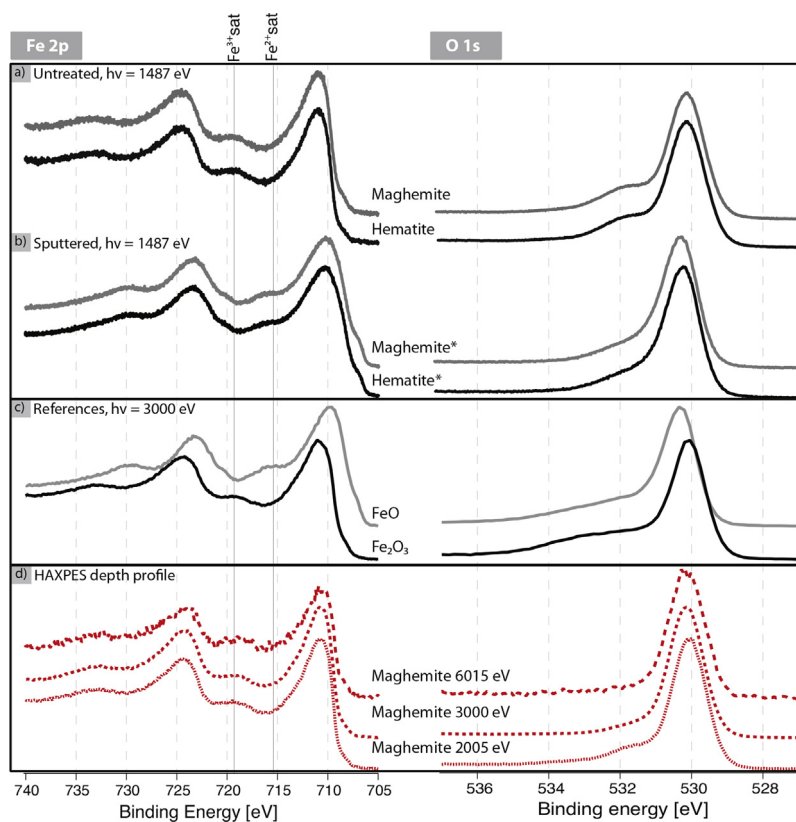


Fig. 2. Fe 2p and O 1s core level photoelectron spectra of maghemite and hematite: (a) untreated, (b) sputtered, and (c) references; (d) HAXPES depth profile data of Fe 2p and O 1s of maghemite. Values in eV designate photon energies. In the case of the sputtered samples (marked with an asterisk) the naming refers to the initial sample.

(d) depth profile data of maghemite recorded with 2005, 3000 and 6015 eV photon energy without any surface treatment.

The overview spectra (Fig. 1) also contain a reference to FTO (substrate). Comparing the maghemite and the FTO it is clear that the maghemite film is a continuous film, since there are no tin peaks visible [15].

The measurements of the single crystalline FeO and Fe₂O₃ (Fig. 2(c)) have well separated spin orbit components. In FeO the positions for the Fe 2p_{1/2} and Fe 2p_{3/2} are located at 723.3 eV and 707.9 eV, whereas for Fe₂O₃ they are shifted towards higher binding energy at 724.3 eV and 711.0 eV. This is in good agreement to reported values by Grosvenor et al. [9]. Other values have also been reported for the FeO and Fe₂O₃ but are not positioned more than 0.2 eV from values presented here [25,26]. The thin solid vertical lines in the Fe 2p spectra indicate the positions of the Fe³⁺ and Fe²⁺ satellites at 719.3 and 715.4 eV binding energy respectively [9]. The reference spectra contains only one of those satellites, thus we can use this as a fingerprint for the chemical state of iron.

Maghemite and hematite have almost identical XPS spectra (Fig. 2a), the difference in lattice structure (cubic vs. hexagonal) having no impact on the chemical shifts. In the unsputtered cases both look akin to the hematite reference spectrum all having a prominent Fe³⁺ satellite [9,26].

Upon sputtering of both the hematite and maghemite there is a shift of the Fe 2p components' binding energies toward lower energies and the satellite structure changes into that of the FeO, visible in Fig. 2(b). This is accompanied by a shift of the O 1s binding energy toward higher binding energy and a lower intensity of the feature around 532 eV binding energy – a region associated with surface hydroxy-groups [26]. Sputtering of maghemite thus acts similarly to heat treatment in vacuum, i.e. as a reducing atmosphere [17]. The sputtered films have a shoulder on the lower energy side of the Fe 2p_{3/2} film that coincides with the low energy shape of FeO.

Argon ion sputtering of iron oxides has been observed to result in FeO rather than metallic Fe, both with hematite and maghemite (Fe₂O₃) and the magnetite spinel Fe₃O₄ [8].

The depth profile obtained by varying the photon energy without changing the sample position (Fig. 2(d)) shows that the maghemite spectral structure of the Fe 2p persists at least down to the information depth (25 nm at 6015 eV, calculated with TPP-2M model [27]), furthermore the high binding energy feature in the O 1s is indeed emanating from the surface as it loses intensity with increasing photon energy. In Fig. 1 the surface exhibits a pronounced roughness, this adds uncertainty to the magnitude of the information depth [28] calculated with the TPP-2M model [27]. The calculated depths are systematically overestimated since the surfaces are not flat, measurements on gold surfaces [29], and SiO₂ on Si [30] with varying roughness suggest that the difference in information depths between the “flat” and the “coarse” surface is approximately a constant, i.e. the different information depths should all be multiplied by an (unknown) factor (<1).

If, having determined the sputtering rate and only the information in the panels (a)–(c) were used, a naïve interpretation would be that our deposited film consisted of a maghemite/hematite over layer (at least 6 nm thick, the information depth at 1487 eV [27]) which is sputtered away, revealing an understoichiometry film beneath, predominantly consisting of FeO.

Besides a shift in the O 1s binding energy towards higher binding energies (+0.2 eV [8,17]) for hematite, the Fe 2p_{3/2} peak-shape has a low binding energy shoulder, as seen in the reference α-Fe₂O₃ spectrum (Fig. 2, panel (c)). McIntyre et al. have the separation of 1.1 eV [8] between the shoulder's peak and the highest intensity peak – for maghemite they do not resolve any such structure. In panel (d) of Fig. 2 we also find that such a two-peak structure is absent for maghemite.

Based on XRD, Raman spectroscopy and HAXPES, we conclude that the films are either maghemite or hematite before the sputtering takes place. It is unlikely that FeO were to be deposited at the chosen process temperature of 300 °C. FeO is metastable below 570 °C and its decomposition leads to metallic iron and Fe₃O₄. The presence of either of those products would dominate the Raman spectrum, since they are much more Raman-active than either Fe₂O₃ phase [23]. Furthermore, metallic iron if present in these kind of films is clearly visible in X-ray diffraction [31]. By neither method decomposition of FeO was observed here.

Using only XPS with Al K α photon energy it would be impossible to discern between maghemite and hematite in the film. The electron mean free path is too short to probe beneath the hydroxy-groups on the surface, and an ion sputtering of the surface would reduce the topmost layer (seen with this λ) to FeO. This Catch 22 can be avoided at higher photon energies: the HAXPES depth profile reveals that the film is homogenous down to 25 nm with hydroxy-groups on the immediate vicinity of the surface.

4. Conclusion

We conclude that great caution must be exercised when sputtering is used to obtain depth profiles, and with the data presented here a clear cut case is demonstrated where ion bombardment sputtering of the surface prohibits a correct interpretation of the film composition. By avoiding sputtering of the surface and increasing the photoelectrons' mean free path with increased photon energy we have been able to assess the composition of the film over a depth range relevant for applications, e.g. iron oxide films on FTO for photoelectrochemical water-splitting have thicknesses in the vicinity of 25 nm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.elspec.2017.09.008>.

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