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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 (γ-Fe_2O_3) and hematite (α-Fe_2O_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 2*p* 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.

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 (α-Fe_2O_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 2*p* 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 Kα). The unsputtered maghemite surface and single crystals of FeO and α-Fe_2O_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 Kα – 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 Kα 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 Kα 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 is present within the substrate and was not observed at the information depth using Al Kα, 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 2*p* and O 1*s* 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 α-Fe_2O_3(0001);

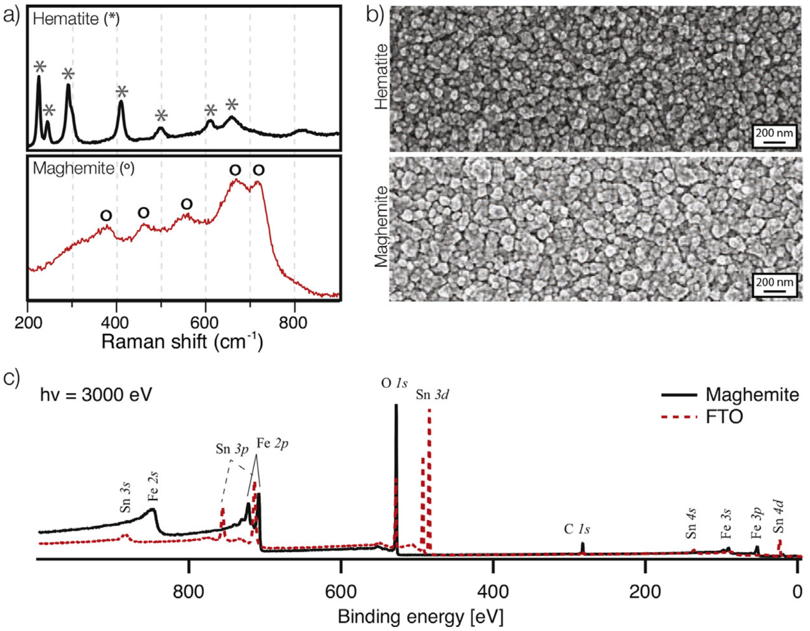

Fig. 1. (a) Raman measurements on the hematite and maghemite films. Panel (b) shows scanning electron micrographs of the nanostructured films. (c) HAXPES measurements of the maghemite film (black) and the FTO used as substrate (dashed).

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