

# Growth of Iron-Oxides on Ag(111)Surfaces

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## INTRODUCTION.

Iron oxide surfaces are of growing interest due to their various catalytic, magnetic and electronic properties. They are used as adsorbents in environmental remediation and in water purification plants owing to their high affinity to ions and molecules (Cornell et al., 2003). In the catalytic dehydrogenation of ethylbenzene to styrene (Zscherpel et al., 1998) iron oxides play an important role. Both magnetic (Prinz, 1995) and non magnetic (Auciello et al., 1998) oxides are being discussed for next generation storage devices. Hematite is a canted antiferromagnet with a high Neel temperature (Morrish, 1995) and may thus be used in magnetic data storage technologies while the half metallic behavior of magnetite raised interest in its potential use in spintronic applications (van der Zaag et al., 2000).

The growth of iron oxide films on metal surfaces is of interest for the study of surface properties by electron spectroscopies and other surface sensitive techniques where charging effects from an insulating substrate have to be avoided. So far most thin films of iron oxides were grown on oxidic substrates like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) (Yi et al., 1999; Chambers et al., 1999) or MgO (manganese oxide) (Kim et al., 1997). As metal substrates only Pt has been used successfully for both hematite and magnetite (Ketteler et al., 2001). There is only one report of the growth of magnetite thin films on Ag(111) (Waddill et al., 2005). The growth of iron oxide films has been reviewed in the past years (e.g. Weiss et al., 2002; Chambers, 2000).

Our results show that depending on the oxygen pressure and film thickness all the three phases of Fe oxides, FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> can be obtained.

## EXPERIMENTAL

Iron oxide films were grown on Ag(111) surfaces by Fe evaporation from Fe-rod in an e-beam evaporator (EFM3 Omicron) and subsequent oxidation in oxygen atmosphere of about  $2 \times 10^{-6}$  mbar O<sub>2</sub>. The deposition rate was calibrated by Auger Electron Spectroscopy (AES) and kept constant by flux control. The iron oxide phases have been characterized in-situ with Low Energy Electron Diffraction (LEED), X-ray diffraction (XRD) and ex-situ by Confocal Raman microscopy. The XRD measurement were carried out in a six circle X-ray diffractometer (Albrecht et al., 1999) using an 18 kW rotating anode and (Cu K $\alpha$ -Radiation). The base pressures of the chambers were below  $10^{-10}$  mbar.

Low lattice mismatch to the iron oxide makes Ag a promising candidate for epitaxial growth and an alternative to Pt(111). The three different phases wuestite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) can be distinguished from the diffraction pattern as they form different superstructures (Fig. 1). The lattice constants of Ag(111) in the hexagonal setting are  $a=b=2.8874\text{\AA}$ ,  $c=7.0728\text{\AA}$ . This makes a lattice mismatch of ~6% for the FeO lattice with  $a=b=3.0589\text{\AA}$ ,  $c=7.4928\text{\AA}$ , and for hematite with  $a=5.035\text{\AA}$ ,  $c=13.747\text{\AA}$  follows a lateral lattice mismatch of 0.7% for the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  superstructure. The lattice constants of magnetite in the hexagonal setting are  $a=b=5.94\text{\AA}$ ,  $c=14.51\text{\AA}$  corresponding to a lattice mismatch of about 3% for a (2x1) superstructure. A projection of the reciprocal lattices in the  $a^*-b^*$  plane is shown in Fig. 1 for hematite and magnetite in relation to the substrate. The points for wuestite nearly coincide with that of silver and are not shown explicitly. All three phases are expected to appear in two domains. The (111) surface of FeO has the symmetry  $p3m1$

of the substrate, but may occur in ABC as well as in ACB stacking which causes a six fold symmetry of the diffraction pattern. The two domains are formed with equal probability. The same argumentation holds true for the magnetite (111) and hematite (0001) surface.

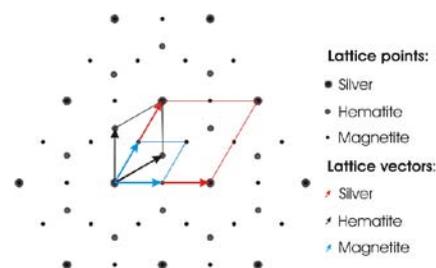


fig 1. The reciprocal lattices for the iron oxides and their relation to the substrate lattice. The lattice mismatch is not considered in this sketch. The wuestite coincides nearly with the silver diffraction spots owing to the small lattice mismatch. The splitting of the spots is not shown.

## RESULTS.

Wuestite and magnetite films were prepared by multiple cycles of deposition and oxidation. Iron was deposited on clean silver substrates with a temperature between room temperature and 150 °C followed by an oxidation period at a pressure of  $2 \times 10^{-6}$  mbar O<sub>2</sub> with temperatures up to 400 °C. The so obtained films (thicker than 10 Å) showed the magnetite structure. Oxidation by a flash to 450 °C in  $9 \times 10^{-6}$  mbar molecular oxygen lead to the formation of hematite.

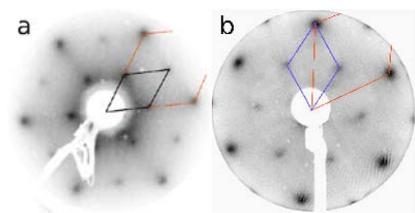
### Wuestite.

Wuestite was identified for films with a thickness <10 Å by XRD and Raman measurements. After iron deposition and oxidation a new peak appears in  $h$  and  $k$  scans over the (1 0) and (0 1)-truncation rod. From the peak position at  $k=0.953$  an in-plane lattice constant of  $3.032\text{\AA}$  was calculated. This is in good

agreement with the bulk lattice constant of 3.059Å. The wuestite phase was confirmed by confocal Raman microscopy.

### Magnetite.

For all magnetite films streaks developed between the silver reflections after oxidation. For thicker films additional reflection spots developed, similar to those presented in Fig. 2 (a) and indicate a magnetite overlayer.



**fig 2.** The reciprocal lattices and lattice vectors for the iron oxides and their relation to the silver substrate lattice. The lattice mismatch is not considered in this sketch. The wuestite coincides nearly with the silver diffraction spots owing to the small lattice mismatch. The splitting of the spots is not shown.

A series of CTR-scans was collected between the evaporation/oxidation steps. The sample was held at 150 °C in  $5 \times 10^{-6}$  mbar of molecular oxygen for 15 min after each deposition step. The strongest peaks originated from the silver Bragg reflections. An increase in intensity of additional peaks corresponding to magnetite could be measured as a function of deposition time.

The symmetry of LEED and XRD results indicate the formation of an epitaxial magnetite film in two domains.

### Hematite.

Magnetite films that were subjected to an oxidation step at 450 °C in  $9 \times 10^{-6}$  mbar  $O_2$  showed substantial changes in their diffraction patterns as well as Raman spectra. An example of a LEED pattern is presented in Fig. 2(b). The pattern shows a hexagonal symmetry, superstructure spots occur at the places expected for hematite (see Fig. 1).

CTR-scans show the disappearance of magnetite reflections while new reflections at hematite positions occur. LEED as well as surface XRD results prove the formation of two independent domains.

To check the degree of transformation

magnetite and hematite reflections were measured before and after the oxidation step. The magnetite peak vanished nearly completely. This proves a profound oxidation of the film. At hematite positions sharp peaks highlight. The relatively narrow peak width measured at the new reflections is an indication for a well ordered film.

Additional measurements show that the film can be reproducibly reduced and reoxidized. At 350 °C in UHV conditions hematite reduces to magnetite. At 450 °C in  $9 \times 10^{-6}$  mbar  $O_2$  the magnetite film can be oxidized to hematite.

### CONCLUSION.

Well ordered iron oxide thin films with thicknesses ranging from a few Å up to thicknesses of 100Å were grown by methods of molecular beam epitaxy by multiple cycles of deposition and oxidation. LEED and XRD were used to study the thin films in situ while Confocal Raman spectroscopy allowed for additional characterization ex-situ.

Wuestite films were formed for films thinner than 10Å after room temperature deposition and oxidation in  $5 \times 10^{-6}$  mbar molecular oxygen and oxidation temperatures of up to 400 °C. This result was confirmed by both Raman spectroscopy and XRD.

For thicker films magnetite could be identified unequivocally by the diffraction techniques. Well ordered magnetite thin films could be grown with a good reproducibility. The films consist of twinned domains due to the  $p3m1$  symmetry of the substrate while the magnetite (111) surface has symmetry  $p3$ . Oxidation temperatures of less than 150 °C with an oxygen pressure  $pO_2$  of about  $2 \times 10^{-6}$  mbar were found to be sufficient for magnetite formation; well ordered surfaces though required annealing to more than 350 °C.

Furthermore, magnetite thin films can be transformed into hematite by flash to 450 °C in  $9 \times 10^{-6}$  mbar of molecular oxygen. The hematite formation was studied by LEED, XRD, and Raman spectroscopy. The oxidation process leads to a nearly complete transformation to hematite. Small islands of magnetite were found by Raman spectroscopy and XRD showed weak intensities for magnetite. The good LEED images are a strong indication for a well ordered surface. Moreover, the

hematite can be reduced back to magnetite by annealing at 350 °C in UHV. SXRD results and the sharp LEED patterns are proof of the conserved epitaxy during these transformations. The diffraction results show that the hematite films consist of twinned domains.

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