

# IRON OXIDES ON AG(111) - REVERSIBLE SWITCHING BETWEEN HEMATITE AND MAGNETITE.

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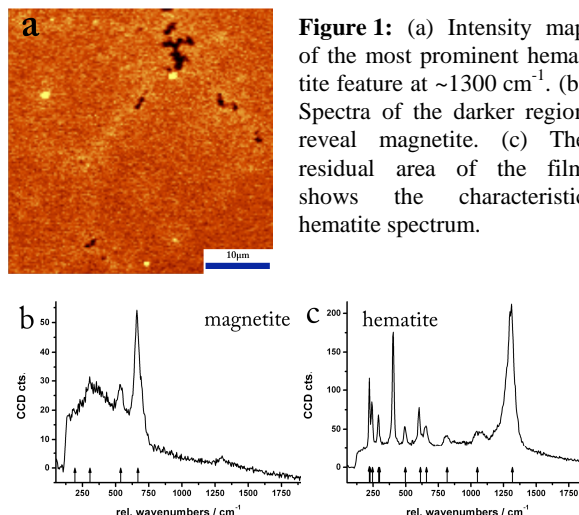
Iron oxides are of growing interest in environmental remediation [1], catalysis [2], magnetic data storage technologies [3, 4, 5] and most recently, spintronics applications [6]. So far, most thin films of iron oxides were grown on oxidic substrates like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) [7, 8] or MgO (manganese oxide) [9]. However, iron oxide films on insulating substrates are subject to charging effects in electron spectroscopies. As metal substrates only Pt(111) has been used successfully for both hematite and magnetite [10]. The low lattice mismatch to the iron oxides makes Ag(111) a promising candidate for epitaxial growth and an alternative to Pt(111). In the literature, only one report of magnetite thin films on Ag(111) was found [11]. Our results show that depending on the oxygen pressure and film thickness all the three phases of iron oxides, wuestite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) can be obtained.

Our iron oxide films were grown on Ag(111) surfaces by multiple cycles of iron deposition (EFM3 Omicron) between room temperature and 150° C followed by oxidation in  $2 \times 10^{-6}$  mbar O<sub>2</sub> at temperatures up to 400° C. Hence, the films were characterized in-situ with Low Energy Electron Diffraction (LEED), X-ray diffraction (XRD), and ex-situ by Confocal Raman microscopy. Thus, the three different phases wuestite, magnetite and hematite can be distinguished from their diffraction patterns as well as their characteristic Raman spectra. The confocal Raman microscope was also used in order to spatially characterize our films.

Wuestite films were formed for films below 10 Å thickness. This result was confirmed by both Raman spectroscopy and XRD. Films of more than 10 Å showed the magnetite structure. The symmetry of LEED and XRD results indicate the formation of an epitaxial magnetite film in two domains.

Oxidation of magnetite films by a flash to 450° C in  $9 \times 10^{-6}$  mbar molecular oxygen leads to the formation of hematite. LEED images indicate a complete transformation to hematite whereas XRD measurements show small quantities of a remaining magnetite structure in the films. Islands of magnetite were found within a matrix of hematite by spatially resolved Raman spectroscopy. Figure 1a shows an intensity map of the second order scattering peak at  $\sim 1300$  cm<sup>-1</sup> only

present for hematite. The dark regions enclosed in this homogeneous hematite film could be clearly identified as magnetite (Figure 1b), while the remaining parts correspond to hematite (Figure 1c).



**Figure 1:** (a) Intensity map of the most prominent hematite feature at  $\sim 1300$  cm<sup>-1</sup>. (b) Spectra of the darker region reveal magnetite. (c) The residual area of the film shows the characteristic hematite spectrum.

Moreover, the possibility of reversible switching between hematite and magnetite was observed. It has been shown that the hematite can be reduced back to magnetite by annealing at 350° C in ultra high vacuum (UHV) conditions. SXRD results and the LEED patterns document the maintained epitaxy during these transformations.

The interplay of diffraction techniques and confocal Raman spectroscopy facilitates the surface phase analysis providing both structural analysis and spatial surface characterization.

**References:** [1] Cornell, R.M. & Schwertmann, U., (2003) *VCH Weinheim*, New York. [2] Zscherpel, D. et al. (1998) *J. Chem. Phys.*, 108, 9506-9515. [3] Morrish, A.H. (1995) *World Scientific*, Singapore. [4] Prinz, G.A. (1995) *Phys. Today*, 48, 58-63. [5] Auciello, O. et al. (1998) *Phys. Today*, 51, 22-27. [6] van der Zaag, P.J. et al. (2000) *J. Magn. Magn. Mater.* 211, 301-308. [7] Yi, S.I. et al. (1999) *Surf. Sci.*, 443, 212-220. [8] Chambers, S.A. & Joyce, S.A. (1999) *Surf. Sci.*, 420, 111-122. [9] Kim, Y.J. et al. (1997) *Surf. Sci.*, 371, 358-370. [10] Ketteler, G. et al. (2001) *Surf. Rev. Lett.*, 8, 661-683. [11] Waddill, G.D. & Ozturk, O. (2005) *Surf. Sci.* 575, 35-50.