



# Surface electronic structure and morphology of silver on iron oxide films

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## ABSTRACT

The surface and electronic structure of silver grown on well defined FeO(111), Fe<sub>3</sub>O<sub>4</sub>(111) and Fe<sub>2</sub>O<sub>3</sub>(0001) films have been in situ studied using various surface analytical techniques. For Ag grown on FeO(111) or Fe<sub>2</sub>O<sub>3</sub>(0001) surfaces, the silver Mie plasmon resonance observed at about 3.8 eV at initial coverage indicates three dimensional growth mode of silver. Contrarily, no Mie plasmon peak detected for Ag on Fe<sub>3</sub>O<sub>4</sub>(111) at initial coverage of Ag suggests a wetting behavior. The main mechanism of Ag growth mode on iron oxide films and the interfacial interaction are discussed. The interfacial information is useful for noble metal–iron oxides system in chemical reactions, e.g. in photocatalysis and biology.

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## 1. Introduction

Oxide supported noble metal systems have been studied intensively due to their extreme importance in catalysis [1–5]. As the earth-abundant and environmentally safe material, iron oxides with unique magnetic and electronic properties are important oxide supports, and have been attracting considerable attention [6–12]. The high Curie temperature (858 K) and the predicted half metallic behavior of magnetite (Fe<sub>3</sub>O<sub>4</sub>) make it useful in spintronics and drug delivery [13]. Water splitting on the surface of hematite (Fe<sub>2</sub>O<sub>3</sub>) has been studied because Fe<sub>2</sub>O<sub>3</sub> is corrosion-stable and inexpensive [3]. Since the interfacial behaviors including the charge transfer, interfacial diffusion play crucial roles on the properties of metal–oxide systems [4,14–16], a detailed understanding of the interface is helpful to improve the performance of real systems in chemical reaction. Thus, model surfaces of single crystals or well-ordered thin films of iron oxides grown on metal substrates including FeO(111) [6,17,18], Fe<sub>2</sub>O<sub>3</sub>(0001) [6,18–21], Fe<sub>2</sub>O<sub>3</sub>(01  $\bar{1}$  2) [22,23], Fe<sub>3</sub>O<sub>4</sub>(111) [6,17–20,24–28] and Fe<sub>3</sub>O<sub>4</sub>(100) [7,29–32] have been studied.

It is known that some surfaces are of polarity [6,33,34]. The polar surface may not be stable and the stabilization of the polar surfaces may lead to different surface structures, which may bring some novel properties. For example, the Jahn–Teller stabilization of polar Fe<sub>3</sub>O<sub>4</sub>(001) results in irreversible water dissociation and the formed surface hydroxyls remain stable up to 500 K [7]. Polarity compensated (1 × 1) surface of 4 nm thick FeO(111) on Pt(111) was prepared with careful optimization of oxidation conditions [17]. The stabilization of FeO(111) may be due to the interlayer relaxation of FeO(111) films [35]. It was reported that the polarity of Fe<sub>2</sub>O<sub>3</sub>(0001) films are

stabilized by strong modification of electronic structure near the surface [6]. As for the Fe<sub>3</sub>O<sub>4</sub>(111) films, strong interlayer relaxation in the surface region makes the polarity compensated [25,26].

Various properties of noble metal particles supported on well-defined iron oxide surfaces were also studied [36–46]. Encapsulation of Pt nanoparticles on Fe<sub>3</sub>O<sub>4</sub>(111) was observed, which is in relation with high adhesion energy between Pt and iron oxide supports [38,40]. The growth modes of Au, Ag and Pt on Fe<sub>3</sub>O<sub>4</sub>(001) and Fe<sub>3</sub>O<sub>4</sub>(111) were discussed based on the surface energy of deposited metals [43,44]. In addition, density functional theory (DFT) calculation shows that the synergistic effects at the interface between the noble metal bilayer and Fe<sub>2</sub>O<sub>3</sub>(0001) support can enhance catalytic activity [46]. Among the noble metals, silver is attractive for industrial applications due to its low cost and easy preparation. Besides the promising application in plasmonic photocatalysts, silver is useful in biological areas because of its good antibiotic properties. For instance, Ag–iron oxides' core/shell nanocomposites have great potential to be applied in targeting therapy area [10–12]. The antimicrobial properties of silver were found to be amplified in partly oxidized silver particles [47]. For silver nanoparticles on iron oxides, however, few model studies have been done and the chemical information, surface electron collective excitation and interfacial interaction are less known.

In the present work, we prepared thin iron oxide films of FeO(111), Fe<sub>3</sub>O<sub>4</sub>(111) and Fe<sub>2</sub>O<sub>3</sub>(0001) on Mo(110) substrate. The growth and electronic structures of silver on these films with different morphologies are investigated by using various surface analytical techniques including low energy electron diffraction (LEED), Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), and electron energy loss spectroscopy (EELS). The experimental results show that, based on the surface plasmon, valence band structure, silver grows on FeO(111) and Fe<sub>2</sub>O<sub>3</sub>(0001) as three dimensional (3D)

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clusters, but forms wetting layer on  $\text{Fe}_3\text{O}_4(111)$ . The reasons for the different growth behaviors are discussed.

## 2. Experiment

The experiments were performed in an ultrahigh vacuum system: ELS-22 (LEYBOLD-HERAUS GMBH) with base pressure of  $2 \times 10^{-10}$  mbar equipped with LEED, AES, high resolution EELS and UPS.

Single crystal of Mo(110) was used as substrate to grow iron oxide films. A C-type thermocouple was spot welded to the substrate for accurate temperature measurements. The clean Mo(110) surface was obtained by annealing at  $\sim 1100$  K in  $\sim 10^{-7}$  mbar  $\text{O}_2$  to remove the surface contamination (mainly carbon), followed by a subsequent flash to 1700 K without  $\text{O}_2$ . No impurities were detected on the substrate by AES except a small residual oxygen signal, which was proved to have no influence on growth of the iron oxide films.

Iron source was made of high purity Fe (99.994%) wire wrapped tightly around tungsten wire. The source was thoroughly degassed by thermal treatment before deposition. The deposition rates of Fe was about 0.5–1.0 monolayer per minute (ML/min) monitored by a quartz crystal oscillator. The FeO(111) films were prepared by evaporating Fe in  $\sim 10^{-7}$  mbar  $\text{O}_2$  at  $\sim 600$  K, followed by annealing at 700–800 K without  $\text{O}_2$ , while  $\text{Fe}_3\text{O}_4(111)$  films were obtained by evaporating Fe in  $\sim 10^{-6}$  mbar  $\text{O}_2$  at  $\sim 600$  K, followed by annealing at 700–800 K without  $\text{O}_2$  [18,24]. The  $\text{Fe}_2\text{O}_3(0001)$  films were obtained by oxidizing the FeO(111) films in  $\sim 10^{-5}$  mbar  $\text{O}_2$  at  $\sim 600$  K for 2 h. The thicknesses of these iron oxide films are estimated to be around 7–15 nm considering the crystal structures and deposition rate of Fe.

Silver was deposited on these iron oxide films at room temperature (RT). The source of silver was made of high purity silver wire (99.995%) either wrapped tightly around tungsten wire or loaded in a fully outgassed alumina crucible. The deposition rate of Ag was monitored by quartz crystal oscillator. The monolayer equivalent (MLE) was used to scale the coverage of deposited Ag with one monolayer packing density being  $1.4 \times 10^{15}$  atoms/cm<sup>2</sup> for Ag(111).

In the UPS measurements, the He I ( $h\nu = 21.2$  eV) source and the pass energy of 4 eV were used. The analyzer takeoff angle is about  $15^\circ$  with respect to the surface normal. The Fermi level ( $E_F$ ) was calibrated using either a clean Mo(110) crystal metal or thick Ni films. Work function of these iron oxide films was monitored by measuring the low energy onset of secondary electron distribution in the UPS spectrum with the sample biased at  $-5$  V. In EELS measurements, primary electron beam energy of 20 eV was used for investigations of surface electronic structures and plasmon excitations. The typical resolution is 60–70 meV from the full width at half maximum of the elastic peak. All data were collected at RT.

## 3. Results and discussion

### 3.1. Preparation of FeO(111), $\text{Fe}_3\text{O}_4(111)$ and $\text{Fe}_2\text{O}_3(0001)$ films

We have systematically characterized as prepared thin films of FeO(111),  $\text{Fe}_3\text{O}_4(111)$  and  $\text{Fe}_2\text{O}_3(0001)$  by using various surface analytical techniques [18]. Fig. 1 shows the AES results. There are only the Auger peaks from Fe MNN, Fe LMM and O KLL in Fig. 1, indicating clean iron oxide surfaces. The Fe/O intensity ratio of these three films agrees well with those of FeO(111),  $\text{Fe}_3\text{O}_4(111)$  and  $\text{Fe}_2\text{O}_3(0001)$  as reported in Ref. [6]. The LEED patterns of FeO,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  films are shown in Fig. 1 as insets. The unit cells indicated in insets all show hexagonal symmetry and correspond to  $(1 \times 1)$  surface unit cells of FeO(111),  $\text{Fe}_3\text{O}_4(111)$  and  $\text{Fe}_2\text{O}_3(0001)$  with surface lattice constant of 3.04, 5.94 and 5.03 Å, respectively [6]. The sharp LEED spots from FeO(111) and  $\text{Fe}_3\text{O}_4(111)$  films are indicative of flatter surfaces. Comparatively, for  $\text{Fe}_2\text{O}_3(0001)$ , the relatively broad spots suggest existence of surface defects.

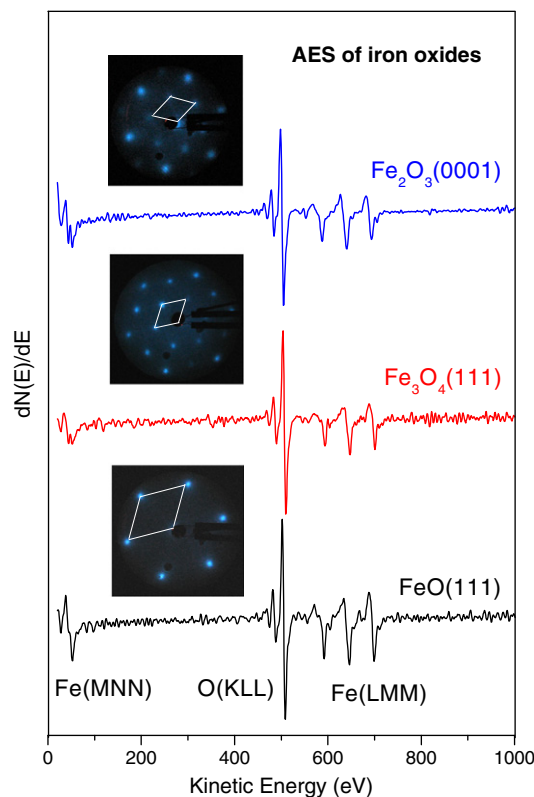


Fig. 1. AES spectra of FeO(111),  $\text{Fe}_3\text{O}_4(111)$  and  $\text{Fe}_2\text{O}_3(0001)$  films. Insets show the corresponding LEED patterns with  $E_p = 61$  eV.

Fig. 2 gives their UPS spectra. In Fe oxides, the valence band consists of overlapping and hybridizing of O 2p and Fe 3d states. The O 2p state is mainly responsible for the most intense emission around binding energy (BE) of 4–7 eV. The characteristic peak at about 1.0 eV is attributed to Fe  $3d^6\bar{L}$  final state inferring  $\text{Fe}^{2+}$  cations, which confirms formation of FeO films [48–50]. For  $\text{Fe}_3\text{O}_4$ , besides the

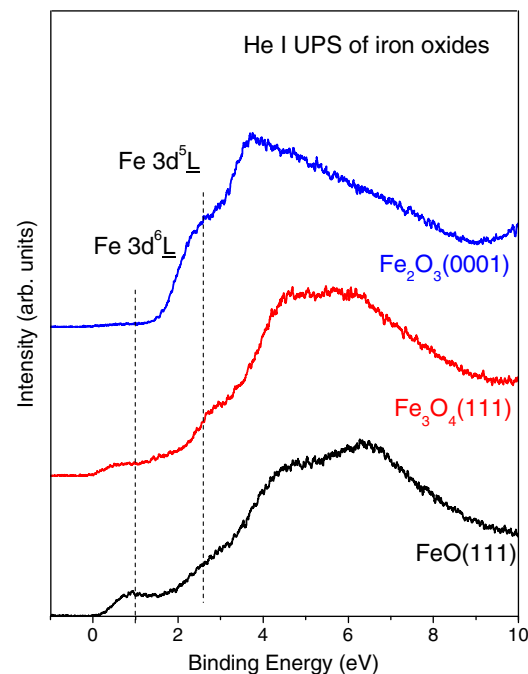


Fig. 2. UPS spectra of FeO(111),  $\text{Fe}_3\text{O}_4(111)$  and  $\text{Fe}_2\text{O}_3(0001)$  films. The dash lines at 1.0 and 2.5 eV correspond to Fe  $3d^6\bar{L}$  and Fe  $3d^5\bar{L}$  final states, respectively.

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