

## XPS and STM studies of gold nanostructures on iron- and oxygen-rich Fe<sub>3</sub>O<sub>4</sub>(001) surfaces

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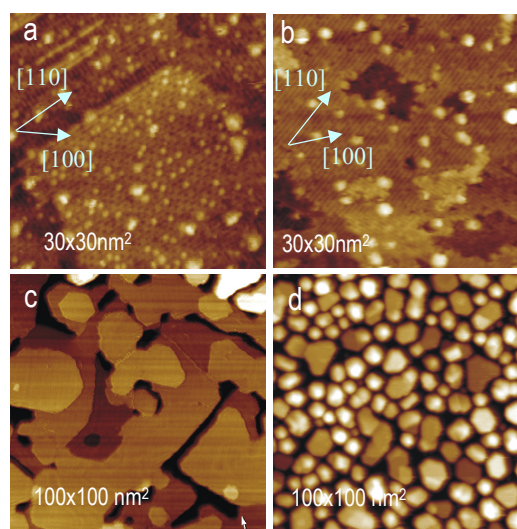
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Gold supported on transition metal oxides is active in the oxidation of CO at low temperatures [1]. The catalytic activity strongly depends on the size of the Au nanoclusters and on their interaction with the oxide support. The present study is focused on correlation between the electronic and geometric structures in the Au - Fe<sub>3</sub>O<sub>4</sub>(001) adsorbate-substrate system.

As the oxide support we were used epitaxial films of magnetite. The film termination could be controlled by a special preparation procedure [2]. The films prepared directly on MgO(001) were terminated with an oxygen-rich layer (the so called B-layer) composed of oxygen and iron ions in the octahedral sub-lattice. Films prepared on an Fe(001) buffer layer were terminated with Fe ions arranged in dimers (the so called A-layer) between rows of the octahedral irons. Fulfilling the neutrality condition, the terminating A-layer is only half-occupied. Both types of surfaces have a  $\sqrt{2} \times \sqrt{2} R45^\circ$  reconstruction as seen by LEED. Even so, the STM measurements clearly revealed differences in the surface structure [2]. Additionally, the X-ray photoelectron spectra (XPS) showed magnetite films prepared on the iron buffer layer have perfect stoichiometry, whereas the films deposited directly on MgO(001) were characterized with a high density of iron vacancies in the octahedral sub-lattice.

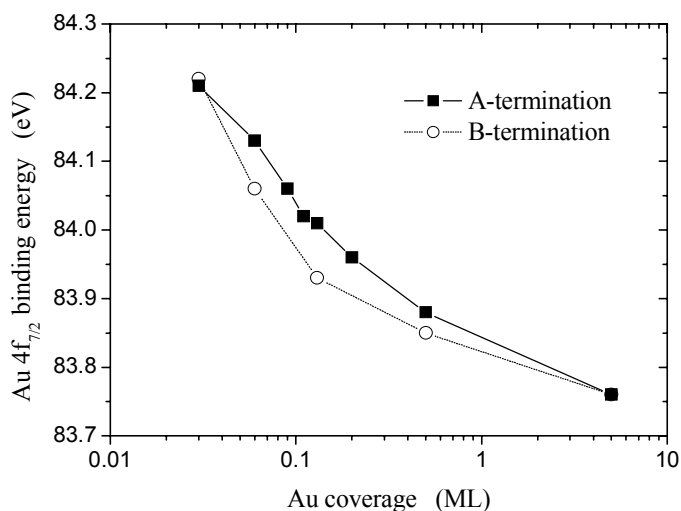
The gold adsorption on Fe<sub>3</sub>O<sub>4</sub>(001) is strongly surface-type specific. Room temperature deposition of Au in the submonolayer coverage range (0.02 - 0.15 ML) on tetrahedrally terminated surfaces resulted in the adsorption of single Au atoms and the nucleation of 2-dimensional clusters (Fig.1 a), whereas only 3-dimensional clusters are stable on octahedrally terminated surfaces (Fig. 1b). The growth differences become apparent for thicker films. On tetrahedrally terminated surfaces, a quasi layer-



**Figure 1** In situ STM images of 0.03 ML, (a,b) and 5ML Au, (c,d) on tetrahedrally (left) and octahedrally (right) terminated Fe<sub>3</sub>O<sub>4</sub>(001) surfaces.

by-layer growth was observed at room temperature for 5 ML of gold (Fig. 1c). This is rather unusual for the Au(111) orientation, as identified from the LEED pattern, taking into account the different symmetries and a large misfit between  $\text{Fe}_3\text{O}_4(001)$  and Au. The observed growth mode results from kinetic limitations at room temperature due to the exceptionally strong metal-support interaction for the particular system. For octahedrally terminated  $\text{Fe}_3\text{O}_4(001)$  surfaces, the island growth of gold with no preferential orientation is observed under the same preparation conditions ( Fig. 1d).

The XPS measurements we made in situ using a R4000 Gammatdata Scienta hemispherical analyser and an unmonochromatized Al  $K\alpha$  excitation source. Surprisingly, for 0.02 ML Au, for which a distinct difference in the Au-adsorbate form was found for both terminations (single atoms versus 3-D cluster), the electron binding energy of the main peak of Au  $4f_{7/2}$  core excitation was found to be 84.2 eV. With increasing Au coverage the Au  $4f_{7/2}$  binding energy of main peak became substrate-termination dependent and decreased faster for the B-termination, as shown in Fig. 2. The lower value of electron binding energy for oxygen-rich magnetite, for the same Au coverage, correlates with STM findings which say that in this case, 3D growth of Au clusters is preferred.



**Figure 2** Dependence of electron binding energy of Au  $4f_{7/2}$  core excitation on Au coverage of A and B terminated magnetite surface.

Detailed analysis of Fe2p and Au4f core excitations in combination with the atomically resolved STM data led to the conclusion that on the A-terminated surface, the gold atoms were adsorbed at  $\text{Fe}^{3+}$  dimers. On the other hand, annealing of the deposited gold nanostructures resulted in exposing  $\text{Fe}^{2+}$  ions on both surfaces.

Support from the Polish Ministry of Science and Higher Education (grant No. 2633/H03/2007/32) is gratefully acknowledged.

## References

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