STM STUDIES OF Au NANOCLUSTERS ON METAL OXIDES

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Introduction
Metal and oxide nanoclusters supported on transition metal oxide surfaces are important catalysts. Precondition for understanding catalytic processes on atomic scale is the knowledge of the atomic level structure and interactions at the cluster-support interface, which can be gained applying surface science approach using to chosen single crystalline model catalysts. The STM archetypal Au/TiO₂(110) system were used to show methodology of the STM cluster analysis, which requires the substrate to be conductive and well defined [1]. Alternative and attractive cluster supports are epitaxial oxide films. Magnetite Fe₃O₄(001) films, exceptional due to their native conductivity, can be easily grown either by reactive deposition or, as shown for the first time presently, by oxidation of epitaxial Fe films. The Fe₃O₄(001) surfaces were used to study gold adsorption and formation of Au clusters.

STM studies of Fe₃O₄(001) surfaces
All discussed samples were prepared on cleaved MgO(001) substrates (for details see [2]). Magnetite films, 20 nm thick, were grown by the Fe-vapor deposition at the rate of about 1 nm/min, in the presence of oxygen, for the substrate held at 520 K. The film stoichiometry was checked ex situ using the Conversion Electron Mössbauer Spectroscopy. As prepared samples displayed a (2 × 2)R45° reconstruction relative the primitive surface bulk unit cell of magnetite (Fig. 1a). Ex situ STM studies of magnetite film require ion bombardment/annealing treatment for restoring the surface cleanness [3,4]. We were able to study the surfaces of the as-prepared films and to examine the influence of annealing as shown in Fig. 1b-d for a 20 nm films. When the films were cooled down to room temperature immediately after the deposition is completed, the STM picture revealed grainy structures with a nanometer lateral size, which by the height analysis can be identified as monoatomic terraces spaced by about 0.2 nm (Fig. 1b). Annealing the films for one hour at the preparation temperature resulted in an increase of the terrace size to several nanometers (Fig. 1c). Rising the annealing temperature up to 800 K produced large
flat areas with the lateral dimensions 20 - 50 nanometers (Fig. 1d). However, improving the surface quality (lateral size of terraces) inevitably leads to the diffusion of magnesium into the magnetite film as checked with AES analysis. This phenomenon sets a temperature limit for the growth of Fe$_3$O$_4$(001) on MgO(001) by the reactive deposition of Fe. An alternative preparation procedure, oxidation of epitaxial ultrathin Fe films [5]. The Fe$_3$O$_4$(001) layer obtained in this way could be subjected to high temperature annealing for improving the structure, because the remaining Fe layer sets an effective barrier for Mg diffusion. Oxidation of 20 nm Fe(001) in 10$^{-4}$ Pa O$_2$ at 250oC, followed by annealing 450 – 500°C result in high quality, impurity free surfaces, for which detailed studies of the surface reconstruction and termination could be performed [6]. Examples of STM surfaces are shown in Fig.2. At a negative sample bias (Fig.2a, occupied states imaged), dimeric feature seen are interpreted as coming from tetrachedral layer. When the bias is changed to positive (Fig.2a, from bottom to top) octahedral layer becomes visible.

**Gold adsorption on Fe$_3$O$_4$(001) surfaces**

Gold supported on transition metal oxides, in particular on non-stoichiometric magnetite is active in cold oxidation of CO [7], which further stimulates Au/Fe$_3$O$_4$ model catalyst studies. Gold adsorption on Fe$_3$O$_4$(001) surfaces described above was studied with in situ STM. Room temperature deposition of submonolayer Au coverages (0.1- 0.2 ML) resulted in ordered single atom adsorption and nucleation of two-dimensional clusters (Fig.3a). At higher coverages Au adsobate forms continues films (Fig.3b) which break to well defined and regular nanometer-sized cluster upon annealing at 350 – 600°C (Fig.3c). Strong metal support interaction is documented by the annealing-induced encapsulation.

Work was supported by the Polish State Committee for Scientific Research, grant no. 7 T08A 002 20.

**References**

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