

Nucleation and growth of Fe and FeO nanoparticles and films on Au(111)

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Abstract

We have studied the formation of Fe and FeO nanoparticles and thin films on the reconstructed Au(111) surface. Scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and ion-scattering spectroscopy (ISS) were used to evaluate the structure and composition of Fe and FeO nanoparticles and films at different growth conditions. Iron grows as one monolayer high triangular particles on the Au(111) reconstruction. FeO was grown by exposing the Fe nanoparticles to molecular oxygen at 323 K, followed by annealing at 500–700 K. XPS results indicate that FeO is formed after room temperature oxidation. STM images show that well-ordered iron oxide particles form after annealing to 700 K. STM images also show evidence of a overlayer lattice with a short periodicity of 3.3 Å modulated by a larger periodicity of approximately 35 Å. The larger periodicity results from a moiré pattern formed between the iron oxide overlayer and the underlying Au(111) surface.

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1. Introduction

The ability to grow controlled nanostructures is important for the development of new materials for catalysis. However, traditional catalytic studies typically use complex and heterogeneous materials which make it difficult to resolve fundamental aspects of adsorption and reaction. By growing nanostructured particles on single-crystal surfaces, we can create a model system to study size and shape effects on reactivity. We can also investigate the effects of defects, such as edge and vacancy sites, on reactivity. Recently, scanning tunneling microscopy (STM) studies have illustrated the importance of using these types of model systems by showing that MoS₂ particles on Au(111) contain edge

sites which are critical for hydrodesulfurization (HDS) reactivity [1].

In recent years, studies on the growth and structure of nanostructured oxide thin films have illustrated the ability to control the structure and composition of these films by varying growth conditions, such as oxidation pressure and temperature [2]. Our approach is to grow model particles and films and to study the structure and composition of these materials using surface science techniques. Studies on these types of nanostructured materials can help us to understand these materials at an atomic level and the importance specific adsorption sites may play in catalysis.

Iron-based catalysts, including iron oxides, are an important class of materials with relevance to Fischer–Tropsch catalysis and gas-sensing applications [3,4]. The growth of iron oxide films on Pt(111) [5–8] and Ru(0001) [9] has been investigated using a variety of surface science techniques. These studies have found that iron oxide forms different phases at high and low coverages of Fe. At coverages of one monolayer (ML), iron oxide forms a film with a

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structure closest to FeO. This monolayer film forms a coincidence structure with the Pt(1 1 1) substrate, resulting in the observance of a superstructure [5]. At higher coverages (thicker films), large, three-dimensional Fe₃O₄ structures were also observed [6,7]. The appearance of Fe₂O₃ structures occurs only after heating the sample to temperatures above 800 °C (1073 K) and exposing the surface to pressures on the order of 10⁻³ mbar of molecular oxygen [10].

The Au(111) surface provides an ideal template to investigate the nucleation and growth of particles due to its inert reactivity and surface reconstruction. To release stress in the Au(111) surface, the Au atoms reconstruct into the well-known “herringbone” reconstruction. This reconstruction is characterized by a (22 × √3) unit cell that contains alternating regions of hexagonal close packed (hcp) and face centered cubic (fcc) stacking sequences [11,12]. A second reconstruction is observed in the formation of zig-zag structures that contain partial surface dislocations in the elbows of the structures at uniform distances apart [13].

Previous work has shown that metals such as Ni [14], Co [15], Fe [16,17], and Ti [18] deposited on the Au(1 1 1) surface nucleate and grow on the elbows of the reconstruction, while other metals such as Ce [19] also accumulate on the step edges. The nucleation of certain metals at the elbows of the reconstruction creates an array of particles that can easily be studied with imaging methods like STM. In many cases, these metal particles can subsequently be oxidized allowing facile STM investigation of the associated metal oxide as was shown for TiO₂ [18] and MoO₃ [20,21]. The reconstructed Au(1 1 1) surface therefore serves as an ideal template to grow arrays of well-dispersed particles.

In this paper we report on the growth of iron clusters and the oxidation of these clusters on the Au(1 1 1) surface. We have used scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and ion-scattering spectroscopy (ISS) to evaluate the structure and composition of Fe and FeO nanoparticles and films at different growth conditions. Our results indicate that a metastable FeO material can be grown on Au(111). Its structure is similar to other FeO materials grown on Pt(111) and Ru(0001) substrates.

2. Experimental

The experiments were performed in a commercial UHV chamber from Omicron Nanotechnology GmbH, equipped with scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and low-energy ion scattering (LEIS). The chamber pressure remained below 5 × 10⁻¹⁰ mbar after degassing. The sample was cooled to room temperature before transferring to the STM. All STM measurements were performed at room temperature in constant current mode using etched W tips from Omicron. Calibration of the STM was performed by measuring the step heights in

images of the Au(1 1 1) surface and comparing them to literature reports [15,22]. Particle size analysis for the STM images was performed using scanning probe imaging processor (SPIP) brand software. The Au(111) sample (Princeton Scientific Corp.) was cleaned by cycles of argon sputtering ($P = 1 \times 10^{-6}$ mbar) at room temperature, and heating to 800–900 K using an e-beam heater. The sample temperature was measured by a Cr–Al thermocouple attached to the manipulator. The sample cleanliness was checked using XPS and STM.

Iron was deposited on Au(111) at room temperature using an electron-beam assisted evaporator (Omicron EFM3T) from a rod material (Goodfellow, 2.0 mm, 99.99%) at 860 V and 7.5 mA (emission). Fe coverage below one monolayer (ML) was estimated by analyzing STM images and the decrease in the Au peak in the ISS spectra. Using the STM images, the relationship between evaporation time and Fe coverage was determined. This relationship was also used to estimate coverages above 1 ML.

In the oxidation experiments, the coverage is notated as a monolayer equivalent of Fe (MLE), which refers to the amount of Fe on the surface before oxidation. Argon and oxygen were introduced into the chamber by backfilling the chamber (Scientific Grade, 99.999%) without further purification. Oxidation at 323 K was performed by exposing the sample to $\sim 3 \times 10^{-7}$ mbar molecular O₂ for 500 s. Afterwards, the sample was heated in vacuum to temperatures of ~ 500 –700 K for 10 min. XPS measurements were collected using an MgK α X-ray source (1253.6 eV). A Shirley background subtraction was performed on the XPS results before further analysis. LEIS measurements were performed with an incident energy of 1 keV He⁺ ($P = 1 \times 10^{-7}$ mbar) ions at room temperature.

3. Results

3.1. Iron growth on Au(111)

The X-ray photoelectron spectroscopy (XPS) of the growth of Fe on Au(1 1 1) at room temperature is shown in Fig. 1. The results show the Fe 2p binding energy as a function of increasing Fe coverage. No noticeable shift in the Fe binding energy from low to higher coverages of Fe/Au(1 1 1) is observed. The binding energy of Fe 2p_{3/2} remains at 706.6 eV, which corresponds to elemental Fe [23]. A satellite shake-up may also be present at ~ 711 eV, contributing to the asymmetric nature of the peak [24]. The Au 4f signal does not exhibit a shift from the clean Au(111) value of 83.8 eV for all of the iron deposition experiments.

A decrease of the Au LEIS intensity, shown in Fig. 1b, indicates that at approximately 0.5 ML Fe, the growth mode of Fe changes, resulting in a slower reduction in the Au LEIS intensity. This decrease is a result of the Fe growing as islands on the Au(111) surface, which will be discussed further in the STM results. At a coverage as high as 5 ML Fe, the Au surface is still detected in the LEIS

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