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STM studies of rhodium deposits on an ordered alumina film-resolution and tip effects

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Abstract

A model system for a dispersed metal catalyst was investigated with STM under UHV conditions. Rhodium metal evaporated on to a well ordered Al_2O_3 thin film support was imaged with STM focusing particularly on the influence of the tip condition on the appearance of the metal islands. A good resolution on top of the aggregates could be achieved reproducibly, whereas a drastic change in the measured lateral size of the particles was found. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Alumina film; Rhodium deposits; STM studies

1. Introduction

With the development of thin film model systems for dispersed metal catalysts [1,2], it has become possible to apply STM to study the morphology and structure of oxide supported metal aggregates. Various details of the growth, such as the temperature-dependent influence of defect sites have become accessible. Even the resolution of atomic features on oxide supported islands has been previously reported [3]. However, with island sizes with widths between 20 Å and 100 Å and heights between 3 Å and 50 Å, the particle dimensions are in the order of the STM tip apex [4–6], and although a good resolution is achieved on top of the metal aggregates, the question of the influence of the tip function on the true geometry of the imaged particles becomes a matter of discussion.

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2. Experimental

We performed the experiments in an UHV AFM/STM(Omicron) system. The sample was mounted on a small molybdenum plate, which could be transferred between the microscope and the main chamber equipped with all instruments necessary for cleaning and preparation of the sample. A NiCr/Ni thermocouple clamped to the sample was used to control the crystal temperature. Its electrical contacts were realised by plug–socket connectors between sample holder and sample plate.

The alumina film was prepared via oxidation of a clean NiAl(110) single crystal surface according to a procedure reported previously [7]. The quality of the film was checked using LEED and STM.

With a commercial evaporator (Focus, EFM 3) based on electron bombardment of a rod, rhodium metal (Heraeus, >99.9%) was deposited on to the sample. To avoid any effects due to Rh atoms

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accelerated towards the sample, it was kept on a retarding potential during evaporation. The nominal film thickness was obtained by microbalance calibration of the evaporator.

3. Results and discussion

In our studies, we used a thin very well ordered alumina film on a NiAl(110) single crystal. This film serves as a support on to which rhodium was evaporated under the control of metal vapour flux and substrate temperature. A change of substrate temperature drastically influences nucleation and growth of the metal. Deposition at 90 K leads to a statistical distribution of metal islands on the Al_2O_3 film. Oxide defects like antiphase domain boundaries have no systematic effect on the nucleation process. At 300 K, these defects clearly dominate nucleation of the aggregates resulting in a decoration of the antiphase domain boundaries and step edges of the oxide film. Both conditions result in the growth of three-dimensional islands [8].

Fig. 1 is an overview of a room temperature deposit of 6 Å Rh on to the ordered Al_2O_3 film.

Between a large majority of disordered aggregates, confirmed by LEED studies, where no additional spots from the ordered rhodium particles could be detected [9], only the STM shows single well-ordered islands with a flat top and a triangular base plane (white circles). The disordered islands appear with a domed top and an irregular shape.

Even though most metal particles have an irregular shape and a height up to 50 Å, details of the topmost layer are imaged reproducibly. Furthermore, atomic steps on top of the ordered islands are clearly resolved. Two triangular aggregates with outlines at 60° with respect to each other are visible in Fig. 1. Various other studies show that such a triangular shape is related to a (111) orientation of the base plane [10–12]. One of these ordered plates shows an interesting detail (Fig. 2). On the flat triangular plateau with an edge length of about 100 Å, another triangle appears. Its orientation with parallel edges to the basis island and the step height of 2.4 ± 0.2 Å (obtainable from a linescan) is in good agreement

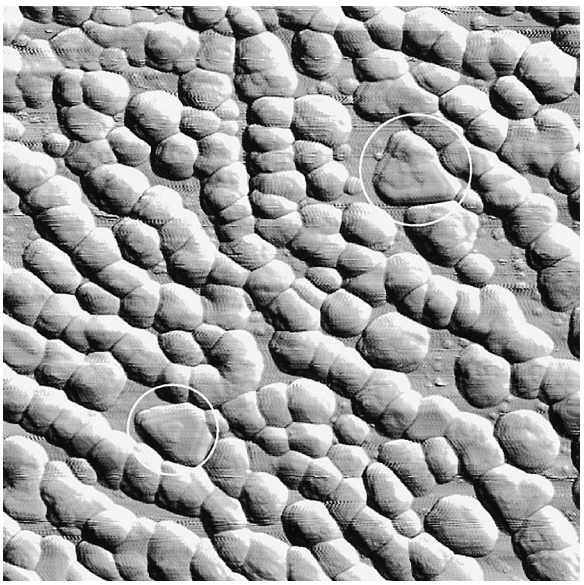

Fig. 1. STM image of Rh deposited at 300 K on the alumina film: 1000 Å × 1000 Å (CCT, $U = 0.9$ V, $I = 1.2$ nA). Two ordered triangular particles (white circles) are visible among the majority of irregular shaped aggregates.

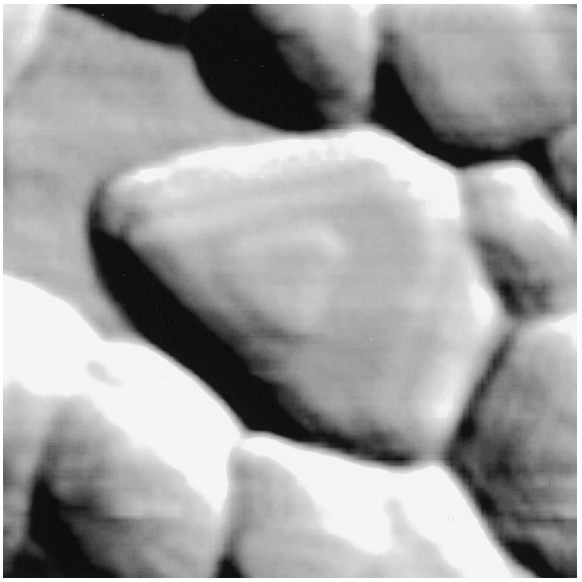

Fig. 2. STM image (close up) of the marked particle (lower left side in Fig. 1). 190 Å × 190 Å (CCT, $U = 0.9$ V, $I = 1.2$ nA). The shape and atomic steps of the topmost layers are clearly resolved.

with the 2.2 Å interlayer distance of Rh [111]. In addition to this, its very regular shape is a good example for a (111)-oriented rhodium monolayer island on a (111)-oriented larger aggregate.

The primary application of STM was the imaging of atomically flat samples [13] with, at most, single atomic steps. In the case at hand, the same situation with the topmost layer (atomic step) on the ordered aggregates (smooth surface) can be considered to exist. Systems consisting of high and steep features, however, as in the case with our dispersed metal model catalysts, cause the imaging mechanism to become more complicated. For flat samples or on top of higher aggregates, only the very end of the tip is responsible for the imaging contact; in systems with higher and sharper elevations, as is the case with imaging the overall geometry and lateral size of an island, a wider range of the tip front is involved in the tunnelling process and therefore contributes to the obtained image [14].

An example of the drastic effect of a tip change on the appearance of the imaged region is shown in Fig. 3. Photographs a and b were taken immediately one after another under exactly identical scanning conditions. Although all parts of the images are very clear and detailed, the apparent island sizes differ drastically after the tip changes. Still, the top layer step edges on single particles are resolved under both conditions (white circles).

Starting the sequence with Fig. 3a (scanning direction from left to right and from down upwards), the tip changed at 30 nm on the y-axis, causing a white line. Something similar obviously happened in Fig. 3b at about 28 nm in the y-direction, also causing a white distortion over the full scan width.

As these tip changes were not accompanied by a wide shift in the scanned region, we now have the situation where the same region is imaged by a tip in a different condition.

Comparing both pictures, it can easily be seen that in one case (lower part of Fig. 3a and the upper part of Fig. 3b), the islands appear larger and only very little uncovered area can be found between the rhodium particles, whereas after the

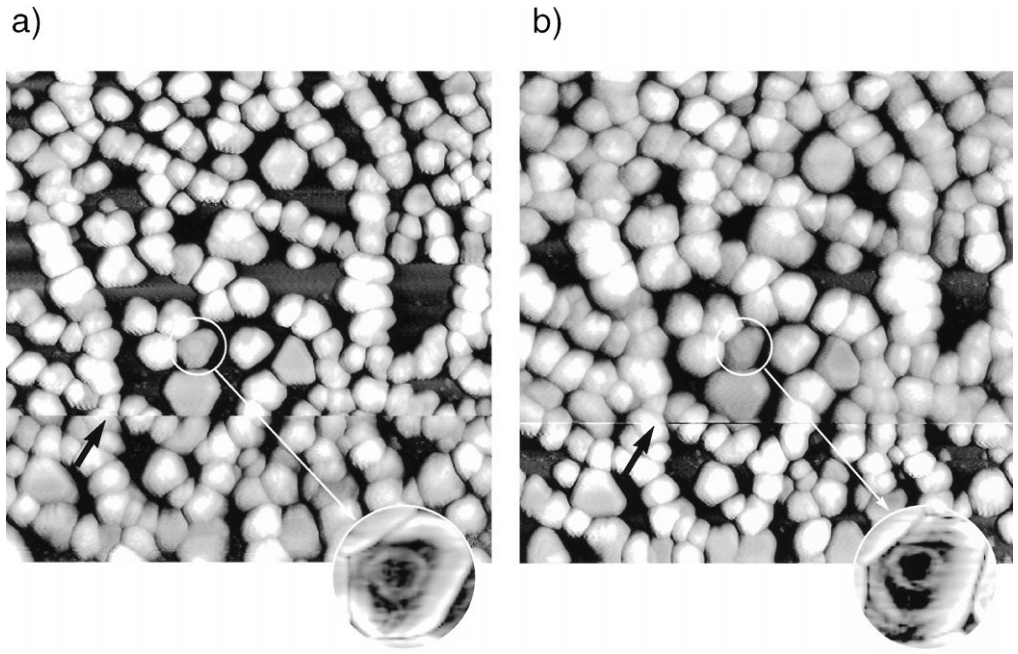

Fig. 3. STM images of 6A Rh deposited at 300 K on the alumina film. 1000 Å × 1000 Å (CCT, $U=1$ V, $I=1$ nA) (valid for both images). The two tip changes are marked with an arrow. An example for the identical on top resolution with both tip conditions is also shown (white circles). The monolayer island is clearly resolved with the same height, geometry and size in both images.

first tip change in Fig. 3a, the particles are smaller, and the uncovered surface increased drastically. All these processes, however, do not change the arrangement, height or the total number of imaged metal particles.

These facts can be easily explained by a change of shape in the tip area that is responsible for the tunnelling signal. As described in the literature [14], extending the radius of the tip front results in an enlargement of the imaged three-dimensional features, as the STM image is a convolution of the true sample geometry with an imaging transfer function that depends on the geometry of the tip. Here, the very end of the tip, responsible for the resolution on top of the particles, seems to be fairly unchanged, whereas the total radius of the tip end obviously increased, resulting in an extended lateral size of the islands at constant height.

4. Conclusion

Although features like step edges and the shape of topmost layers are resolved reproducibly from the STM tip, which is a good indication for a sharp tip end, for the appearance of the overall geometry and lateral size of the metal particles, a wider range of the tip is responsible. A change of this region obviously can occur easily not affecting the resolution on top of the islands but heavily influencing the imaged lateral dimension of the particles. None of these changes in the tip geometry changes the arrangement or total number of the imaged islands so that an investigation, for example, of defect influence on the growth mode of a system or the evaluation of island densities is not affected.

However, the evaluation of these systems with high and disordered aggregates concerning total coverage of the surface with deposited metal only based on STM images seems to be problematic, and it would be necessary to obtain additional information from complementary methods like electron diffraction.

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