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Crossover from Three-Dimensional to Two-Dimensional Geometries of Au Nanostructures on Thin MgO(001) Films: A Confirmation of Theoretical Predictions

Martin Sterrer,* Thomas Risse, Markus Heyde, Hans-Peter Rust, and Hans-Joachim Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Chemical Physics, Faradayweg 4-6, D-14195 Berlin, Germany

In this Letter, we report a low-temperature scanning tunneling microscopy study aiming to explore the adsorption properties of Au with respect to the thickness of supported MgO films. For different MgO film thicknesses (3 ML and 8 ML), we find significant differences in the distribution of Au adsorption sites and in the Au cluster geometry, in line with recent calculations and electron paramagnetic resonance experiments. On the surface of thick MgO films or unsupported MgO, Au adsorbs on O sites [Phys. Rev. Lett. **96**, 146804 (2006)], and the equilibrium cluster geometry is three-dimensional. In contrast, on thin MgO films, the calculations predicted (i) a change of the preferred Au nuclation site [Phys. Rev. Lett. **94**, 226104 (2005)] and (ii) a stabilization of two-dimensional Au cluster geometries [Phys. Rev. Lett. **97**, 036106 (2006)].

Tuning the performance of heterogeneous catalysts based on a microscopic understanding of their physical and chemical properties is a long-standing goal of research in heterogeneous catalysis [1]. Despite the efforts made in the last decades and the progress achieved in this respect, design of real catalysts is still largely based on empirical knowledge and chemical intuition. On the other hand, the development of methodology to prepare and characterize model systems of heterogeneous catalysts to unprecedented accuracy has opened new opportunities not only to provide microscopic insight into various aspects of heterogeneous catalysts, but also to check existing or look for new concepts by appropriately designing the system.

In recent years, thin oxide films grown on metal single crystal surfaces have proven to be suitable substrates to prepare model catalysts resembling the complexity of the real system reasonably while allowing a rigorous characterization by means of modern surface science techniques [2–6]. A key question for these systems from the very beginning was the ability of the films to appropriately mimic the properties of the bulk oxides usually used in real catalysts. It was shown that this is often fulfilled. However, there are a few systems were this presumption breaks down because of the small thickness and the particular electronic and geometric properties of the well ordered oxide films, which may influence the adsorption behavior, e.g., of metal atoms and clusters [7–9]. To this end, it is interesting to elucidate if such qualities that have been found for several ultrathin oxide films can be used to tune the properties of adsorbates [10].

This idea has been put forward by recent density functional theory (DFT) calculations. For gold adsorbed on thin MgO films in particular [11–13], but also for other systems [13–15], these calculations have shown that for a proper combination of materials, the properties of adsorbates may continuously change as a function of film thickness due to enhanced charge transfer between substrate and adsorbate as the oxide film thickness is decreased. An experimental

realization of this concept is, however, frequently hampered by the fact that a continuous change of the film thickness is often not achievable or an appropriate methodology to probe the expected changes is not easily available.

To address the impact of film thickness on the properties of adsorbates, we use low-temperature scanning tunneling microscopy (STM) to study the properties of gold atoms and clusters adsorbed on MgO films in thickness regimes where either bulklike or strongly modified adsorption behavior is expected, respectively. Thin MgO films supported by Ag(001) are particularly suited for studying the film thickness dependence due to the small lattice mismatch between Ag(001) and MgO(001), which allows homogeneous film growth in a wide thickness range [16]. Recent investigations have shown that the pseudomorphic growth of MgO on Ag(001) induces some strain in the film which is completely released for film thicknesses greater than 7 ML [16]. In the studies reported herein, a 3 ML thin MgO film was already sufficient to exclude an influence of film growth related imperfections for the adsorption properties of Au atoms. We have studied the adsorption behavior of gold on such thin MgO films and compare the results with those obtained for Au adsorption on thicker films (8 ML) with respect to adsorption geometry and cluster formation. Our results clearly show that the adsorption properties of Au on 8 ML thin MgO films resemble essentially the situation for adsorption on MgO(001) bulk, whereas the adsorption behavior is strongly modified on 3 ML thin MgO films, as recently proposed by DFT calculations [11,12].

Magnesium oxide thin films were prepared by reactive deposition of Mg in an oxygen ambient using a Ag(001) substrate. The Ag(001) single crystal was cleaned by repeated sputter (Ar$^+$, 10 μA/cm^2) and anneal (700 K) cycles. Mg was deposited on Ag(001) from a UHV evaporator at an oxygen pressure of 1×10^{-6} mbar and a substrate temperature of 570 K. The MgO growth rate was 1 ML/min. The experiments were performed in a custom-

built low-temperature STM operating at 5 K [17]. Under our experimental conditions, stable tunneling could be maintained for MgO films of 8 ML thickness. Au atoms were evaporated onto the MgO films in-situ in the STM compartment at a sample temperature of 5 to 10 K. Cluster formation of Au was induced by annealing the sample to different temperatures.

In Figs. 1(a) and 1(b), STM images of Au atoms deposited at a substrate temperature of 5–10 K on 3 ML and 8 ML thin MgO films, respectively, are shown. In both cases, the Au coverage is about 0.035–0.040 ML, and single Au atoms are imaged as bright spots. The STM images reveal an ordering of the adsorbed Au atoms on both MgO films indicating significant adatom interaction. This observation implies that during deposition, the barrier for diffusion of the gold atoms on the surface of the thin MgO films can be overcome, leading to transient mobility and the formation of a superstructure that is mainly driven by the adatom interactions. Evidence for this effect comes from the coverage dependence of the nearest-neighbor (NN) distance distribution of Au adatoms shown in Fig. 1(c) for the case of Au deposited on 8 ML MgO/Ag(001). The maximum of the NN distance distribution corresponds well with the expected NN distance for a perfect hexagonal array of adatoms for the coverage regimes investigated. The small

FIG. 1 (color online). STM images (25 nm × 25 nm) of Au atoms ($\theta \approx 0.035$–0.040 ML Au) deposited at 5–10 K on (a) 3 ML MgO/Ag(001) and (b) 8 ML MgO/Ag(001), respectively ($V_S = +0.5$ V, $I_T = 10$ pA). (c) Comparison of the coverage dependent nearest-neighbor (NN) distance distribution for Au adatoms adsorbed on 8 ML MgO/Ag(001) and the corresponding calculated NN distance for a perfect hexagonal superstructure with the same coverage.

deviation between experimental and theoretical NN distance at the highest coverage investigated [0.043 ML, Fig. 1(c)] results from the presence of Au aggregates.

Recently, ordering of Au atoms on a 3 ML thin MgO film has been studied [18]. Based on DFT calculations, the ordered structure was attributed to the repulsive interaction between charged Au atoms. The charge transfer from the substrate to the Au atoms is particularly important for very thin MgO films [11,13], while Au atoms on thick films (20 ML) or bulk single crystals are highly polarized but essentially neutral [19]. The question arises whether the ordered arrangement found for both film thicknesses has the same physical origin, namely, the repulsion of charged metal atoms, or if the Au atoms on 8 ML films exhibit a different binding behavior indicating that the mechanism for the ordering may also be different. To find evidences for such a different binding mechanism, it is worthwhile to have a closer look into the physical origin for the charge transfer on thin films of a thickness of a few layers. DFT calculations show that charged Au atoms on 3 ML MgO films are stabilized by strong polaronic distortions of the MgO film [13]. The polaronic distortions together with the charge transfer towards the Au atoms do not only change the adsorption energy, but they also lead to significant modifications of the adsorption geometry. While on bulk MgO or thick films Au atoms are expected to nucleate on top of oxygen ions (adsorption energy $E_A \approx 1.0$ eV on O vs $E_A \approx 0.5$ eV on Mg) [11,20,21], a strong stabilization of Au on Mg sites in combination with an increased absolute binding energy is found for films with a thickness of a few monolayers [$E_A \approx 1.9$ eV on Mg vs $E_A \approx 1.6$ eV on O for 3 ML MgO/Mo(100) and $E_A \approx 1.52$ eV on Mg vs $E_A \approx 1.46$ eV on O for 2 ML MgO/Ag(100)] [11,13]. The stabilization on Mg sites results from the Coulomb attraction between the positively charged surface Mg ions and the negatively charged Au atoms. The adsorption behavior on thick (20 ML) MgO films was recently verified using electron paramagnetic resonance (EPR) spectroscopy [19].

In order to obtain direct evidence for differences in the adsorption properties of Au on MgO films of different thickness, an attempt was made to determine the adsorption sites of Au on the surface of the 3 ML and 8 ML thin MgO films, respectively. Unfortunately, it was not possible to obtain atomically resolved images for surfaces of adsorbed Au atoms on MgO films. Instead, atomically resolved images of 3 ML and 8 ML MgO films acquired prior to Au deposition [Fig. 2(a)] were used to deduce information on the adsorption sites by superimposing the obtained surface (sub-)lattice on STM images obtained after deposition of Au on these surfaces [Fig. 2(b)]. The evaluation of the data allows extracting the ratio of atoms adsorbed on site 1 to those on site 2, with 1 and 2 being either O or Mg. Figure 2(c) presents the results for the distribution of Au adsorption sites obtained from a series of measurements for Au atoms on 3 ML and 8 ML thin MgO films, respectively. Assuming adsorption on both Mg and O sites being possible, we obtain an almost equal probability for Au adsorp-
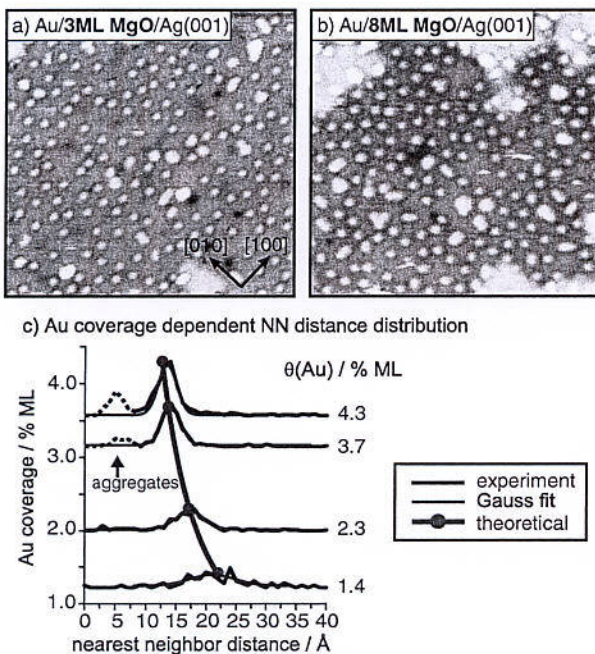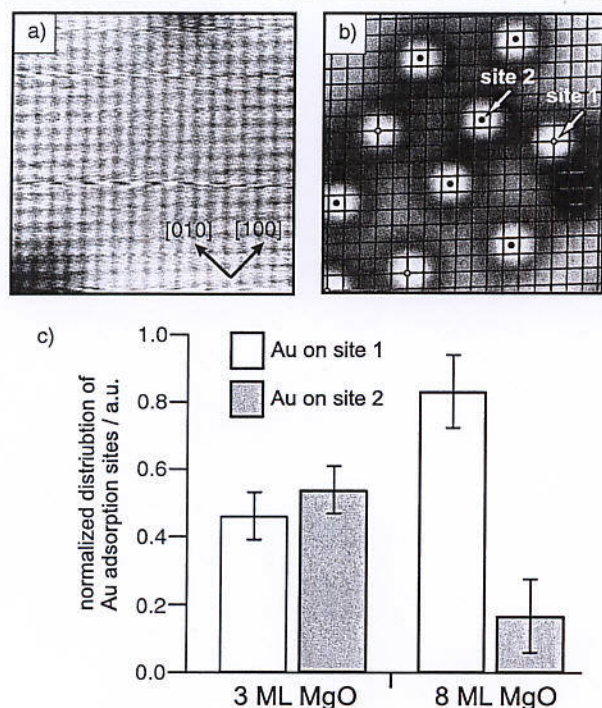
FIG. 2 (color online). (a) Atomically resolved STM image (5 nm × 5 nm) on 3 ML MgO/Ag(001), $V_S = +0.02$ V, $I_T = 7$ nA; only one ionic sublattice is resolved. (b) STM image (5 nm × 5 nm) of Au atoms deposited at 5–10 K on 3 ML MgO/Ag(001), $V_S = +0.5$ V, $I_T = 10$ pA; the ionic sublattice extracted from (a) is superimposed revealing the different adsorption sites. (c) Distribution of adsorption sites for Au on 3 ML and 8 ML thin MgO films, respectively.

tion on these two sites on the surface of a 3 ML MgO film. In contrast, for Au adsorption on the 8 ML MgO film adsorption on one particular site is always preferred [Fig. 2(c)].

It is important to mention at this point that the metal deposits prepared here are not in thermodynamic equilibrium. As mentioned above, transient mobility during the deposition process enables the Au atoms to diffuse on the MgO surface. The nucleation site for the Au atoms, therefore, depends on the residual energy the Au atoms carry after several hops and on the potential landscape of the surface. Thus, it is to be expected that the adsorption site distribution shown in Fig. 2(c) does not reflect the nucleation probabilities of the different sites based on thermodynamic considerations, but is determined by kinetic effects. Recent DFT calculations have shown that the diffusion barriers for Au atoms are considerably smaller on ultrathin MgO films as compared to bulk MgO(100) [13]. This, together with the almost similar adsorption energies for Au adatoms on Mg and O sites on thin MgO films [13], could lead to the almost equal distribution of Au atoms on Mg and O sites in our experiment on 3 ML thin MgO films. Based on the cumulative theoretical and experimental

knowledge that Au atoms nucleate on top of oxygen on the surface of thick MgO films or bulk MgO single crystals [11,19–21], it is inferred that the majority of Au atoms adsorbed on the 8 ML thin MgO film nucleate on oxygen ions.

The change of preferred Au adsorption sites on the MgO surface indicates that the adsorption behavior of Au atoms is significantly altered for film thicknesses between 3 and 8 ML. To find further experimental proof for these differences the temperature induced agglomeration and cluster formation of Au on the surface of thin MgO films was studied. In Figs. 3(a) and 3(b), STM images obtained after annealing the samples with Au atoms deposited on 3 ML and 8 ML thin MgO films, respectively, to 210 K are shown. A comparison of these images already reveals a qualitative difference between the two situations: On the 3 ML thin MgO film, the annealing to 210 K yields extended two-dimensional islands that wet the MgO surface [Fig. 3(a)], whereas Au particles of different height are formed on the 8 ML thin MgO film [Fig. 3(b)]. This difference becomes more apparent by increasing the annealing temperature to 300 K. After this annealing step, the Au islands on the 3 ML MgO film remain two-dimensional [Fig. 3(c)] while structured three-dimensional clusters, comparable to those found after Au deposition on MgO(100) single crystals [22–24], are observed on the surface of the 8 ML thin MgO film [Fig. 3(d)].

Figure 3(e) shows the profiles of representative Au particles found for the different preparation conditions as indicated by the white lines in Figs. 3(a)–3(d). For Au particles on an 8 ML MgO film, the apparent height increased from 4 Å after annealing to 210 K to 6 Å after annealing to 300 K, consistent with the growth of three-dimensional clusters. In contrast to the three-dimensional clusters observed on 8 ML MgO films, the apparent height of the Au islands on the 3 ML MgO films is 2 Å both after annealing to 210 K and 300 K, corresponding to mono-atomically flat islands. This result is perfectly in line with recent DFT calculations on the geometry of Au clusters adsorbed on MgO(100) and thin, Mo-supported MgO films, showing that two-dimensional clusters are preferred on supported MgO films up to a film thickness of several ML, while three-dimensional clusters are expected for bulk MgO single crystals [12]. The experimental results presented here show that this *crossover in dimensionality* from planar to three-dimensional Au clusters occurs for MgO film thicknesses between 3 ML and 8 ML.

The differences observed for the adsorption site probabilities as well as in the annealing behavior indicate that the binding of Au atoms differs significantly between MgO films of 3 ML or 8 ML thickness. In particular, the Au adsorption properties of the 8 ML films resemble those of bulk MgO single crystal surfaces to a large extent. Based on these observations, it is justified to conclude that the ordering of Au atoms observed for the 8 ML films [Fig. 1(b)] has a different origin than the one observed on the 3 ML film [Fig. 1(a)] which was explained by Coulomb
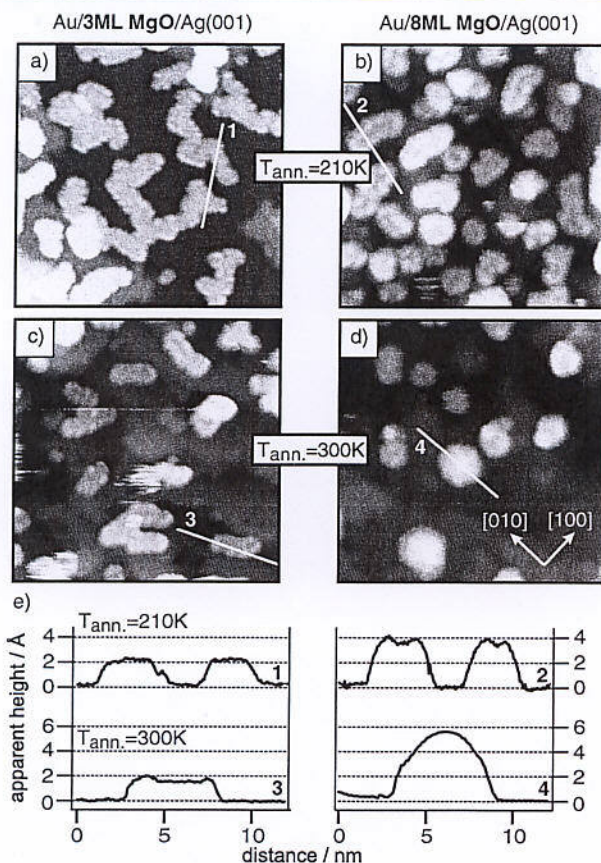
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FIG. 3 (color online). STM images (30 nm × 30 nm) of Au clusters formed after annealing Au atoms deposited on 3 ML and 8 ML thin MgO films, respectively, to $T_{ann.} = 210$ K (a,b) and $T_{ann.} = 300$ K (c,d), $V_S = +0.5$ V, $I_T = 10$ pA. (e) Height profiles of Au clusters marked with a white line in Figures 3a–3d.

repulsion between the charged metal atoms. Au atoms on thick MgO films were shown to be essentially neutral but strongly polarized [19]; thus, it is proposed that the observed order is induced by the dipole-dipole interaction of the strongly polarized atoms.

In summary, we have presented a detailed experimental study elucidating the influence of oxide film thickness on adsorption properties using Au atoms on single crystalline MgO films as an exploratory system. The adsorption of Au on supported MgO is found to be strongly influenced by the metallic substrate in the limit of thin MgO films and approaches bulklike properties with increasing MgO layer thickness. In particular, on an 8 ML thin MgO film, Au adsorbs preferentially on oxygen sites and annealing to room temperature yields three-dimensional clusters, resembling essentially the situation encountered for Au adsorption on the MgO(001) surface. In contrast, Au adsorption takes place both on magnesium and oxygen sites and, after annealing, clusters stay two-dimensional on a 3 layer MgO film. These results support the suggestion that the properties of Au atoms and clusters can be tuned by

the MgO layer thickness, with the tuning range being between the two limiting cases studied here, 3 ML and 8 ML thin MgO films. In particular, the ability to produce charged gold atoms and two-dimensional Au islands on thin MgO films might be of potential interest in future studies on the chemical reactivity of these systems [25].

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Note added in proof.—In a recent theoretical paper [26], hollow site adsorption was found to be preferred for ultra-thin MgO films. Our experiments on 3 ML MgO films are compatible with this finding; however, this does not change the conclusion of different adsorption sites on 3 and 8 ML films.

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*Electronic address: sterrer@fhi-berlin.mpg.de

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