P H Y S I C A L   R E V I E W   L E T T E R S

Control of the Charge State of Metal Atoms on Thin MgO Films

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The arrangement of single gold and palladium atoms deposited on the surface of a 3 monolayer thin film of MgO was investigated using low-temperature scanning tunneling microscopy. While Pd atoms are arranged in a random fashion, Au forms an ordered array on the surface. The long-range ordering as well as the scanning tunneling microscopy appearance of single Au atoms on a 3 monolayer thin MgO film can be explained by partial charge transfer from the substrate to Au atoms as predicted recently by density functional theory calculations [Phys. Rev. Lett. **94**, 226104 (2005)]. In contrast with that, Au atoms on a thick film were found to be essentially neutral.

PACS numbers: 68.43.Fg, 68.37.Ef, 68.47.Gh, 73.61.−r

The identification of concepts which allow understanding and subsequently tuning the catalytic properties of heterogeneous catalysts is still one of the key issues of research in catalysis. A variety of different strategies have been put forward over the past decades in the effort to compass and establish a rational design of heterogeneous catalysts [1]. Most of these strategies are based on structure reactivity relationships, taking different aspects of the exceedingly complex systems into account. To this end model systems using metal particles supported on well ordered thin oxide films of appropriate thickness, which allow investigations with the rigor of modern surface science while grasping essential aspects of the complexity of real systems, have proven to give valuable insight into the details of geometric and electronic structure, as well as adsorption and reaction properties [2–6].

It has been recognized that the thickness of the oxide films, as they are grown on metal substrates, may be used as a design principle to create materials of potential in catalysis. A concept to control the catalytic activity of a dispersed metal by the thickness of an insulating oxide layer was introduced some 20 years ago by Cogen *et al.* using silica layers covering Pt [7]. In this case the catalytic performance for dehydrogenation of cycloalkenes depends significantly on the thickness of the silica films, which was explained by the decreasing transport of hydrogen atoms produced at the Pt surface through the silica film. The main experimental challenge, however, is to provide undisputable proof for the proposed mechanisms which is usually hampered either by the complexity of the samples investigated and/or the lack of appropriate methodology to exclude interference with alternative mechanisms. Having ultimate control, as available today, over the thickness and structure of the oxide films, these properties may be used to control the charge state and, thus, the catalytic properties of a metal deposited onto them, an idea related to those proposed by Cabrera and Mott in connection with metal oxidation [8].

Early on it was realized that particular sites of a thin oxide film support can provide means to alter the properties of deposited metals. In particular, oxygen vacancies have come under scrutiny since combined experimental and theoretical investigations of Au clusters on MgO surfaces point towards the importance of such point defect sites for the catalytic properties of deposited Au clusters due to their ability to donate charge to the metal clusters [9]. It was not until recently that the correlation between presence of color centers and their impact on the properties has been directly verified [10].

However, charging of adsorbed metals must not necessarily involve the presence of defects on the oxide surface: on the basis of density functional theory (DFT) calculations it was proposed that charge transfer may also occur for metal atoms and clusters adsorbed on a supported thin oxide film, provided that the adsorbed metal exhibits a high electron affinity and the film thickness does not exceed a few monolayers (ML) [11–13]. In particular, Au atoms adsorbed on a thin MgO film grown on Mo(001) and Ag(001) are expected to be negatively charged in contrast to their counterparts on bulk MgO (or thick MgO films), which were proven to be essentially neutral [14]. Thus, the thickness of the oxide layer may serve as a parameter to tune the electronic properties of supported metals. In the following we apply low-temperature scanning tunneling microscopy (STM) to obtain firm experimental evidence for such a mechanism by comparing the adsorption behavior of single Au and Pd atoms on 3 ML thin MgO films supported on Ag(001).

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 $(Ar^+, 10 \ \mu A \cdot cm^{-2})$/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 $1 \ ML \cdot min^{-1}$. The experiments were performed in a

custom-built low-temperature STM operating at 5 K [15]. Au and Pd atoms were evaporated from a hot filament ($T \approx 1000$ K) at a deposition rate of 0.1 ML · min^{-1} and a sample temperature of 5 to 10 K. DFT calculations of the STM images are based on the PW-91 exchange-correlation functional [16] and the VASP program [17,18] (see Ref. [13] for details). 3 ML MgO have been deposited on four Ag layers representing the Ag(100) substrate. Since the Ag lattice constant ($a_0 = 4.16$ Å) is 2% smaller than the MgO one ($a_0 = 4.25$ Å), the MgO layers are slightly contracted. During geometry optimization, all atoms in the MgO film and in the two surface nearest Ag layers were relaxed while the remaining two metal layers were frozen at bulk positions.

Figures 1(a) and 1(b) show STM images (30 nm × 30 nm) of Au and Pd atoms, respectively, evaporated on a 3 ML thin MgO film at a substrate temperature of 5– 10 K. For the coverage of $\Theta = 2$–3×10^{-2} ML single metal atoms, imaged as bright protrusions for the given tunneling conditions, are the predominant species on the surface, while aggregates and clusters play only a minor role. The bright squarelike features in the STM images originate from MgO ad-islands. A qualitative inspection of Fig. 1(a) reveals that Au atoms are evenly distributed on the surface with rather well defined nearest-neighbor distances, which is an indication for strong adatom interactions. In contrast, Pd atoms [Fig. 1(b)] deposited at the same conditions exhibit a more or less random distribution. Thus, the electronic properties of the adsorbed metal atoms and their interaction with the thin MgO film play an important role for the observed nucleation behavior. To ensure that the ordering of Au atoms on thin MgO films is not mediated by interactions with the metal substrate, such as coupling to surface states or Friedel oscillations [19,20], Au atoms were also deposited on bare Ag(001). This situation, shown in Fig. 1(c), reveals a random distribution of Au atoms indicating that the thin MgO layer plays an essential role for the observed ordering of Au atoms on MgO/Ag(001).

In an attempt to quantify the adatom interactions, the radial pair distribution function, $f_{exp}(r)$, was determined from the STM images by counting for each atom the number of neighbors found in a ring of inner diameter r and width Δr. This radial distribution function is compared to the theoretical expectation for a random occupation of sites, $f_{rand}(r)$, given by

$$f_{rand}(r) = (2\pi r \Delta r N^2 / L^2)([\pi L^2 + (4 - \pi)r^2 - 4rL]/\pi L^2)$$

for N ($= L^2\Theta/A_{unitcell}$) atoms in an STM image of size $L \times L$ [20]. The first term describes the probability of finding pairs of adatoms separated by a distance r to a distance $r + \Delta r$, and the second term accounts for the finite size of the STM image. Figure 2 shows the normalized radial distribution function, which is given by the ratio $\rho = f_{exp}(r)/f_{rand}(r)$, for the three examples considered in this study. For Pd/MgO(3L)/Ag(001) [Fig. 2(b)] and Au/Ag(001) [Fig. 2(c)] the distribution of adatoms can perfectly be described by a random site occupation since $\rho \approx 1$ for all distances r. In contrast, for Au atoms on a 3 ML thin MgO film the normalized radial distribution function shows substantial deviations from random site occupation up to $r = 40$–50 Å [Fig. 2(a)]. The oscillatory behavior of ρ around 1 is typical for ordered structures on surfaces and points to long-range adatom interactions [21–23].

In case of thermal equilibrium between substrate and adatoms the interaction potential can be derived from the corresponding distance distributions using Boltzmann statistics [23]. However, the present experiments represent a nonequilibrium situation and we, therefore, restrict the discussion to a qualitative interpretation of the results. The observed ordering of Au atoms on the 3 ML thin MgO(001) film is caused by a long-range repulsive interaction between the adatoms. This is evidenced by a negligible probability of finding pairs of adatoms with separations in a range ≲10 Å. The first maximum seen in the normalized radial distribution function [Fig. 2(a)] at $r = 16$ Å for the given Au coverage is indicative for the high probability to find the nearest-neighbor adatom at this distance. (For comparison, a perfect hexagonal array of adatoms with the same coverage would yield a nearest-neighbor distance of 15.5 Å.) A smaller, but still recognizable maximum at $r = 32$ Å is found for the next nearest-neighbor distance indicating a two-dimensional long-range order of adatoms.

What is the reason for this long-range interaction? Recently, ordered structures of metal atoms have been observed on other thin oxide films. On a thin alumina film on NiAl(110) gold atoms were found to adsorb preferentially along the main crystal directions of the metallic substrate leading to a one-dimensional ordering, which indicates the particular importance of the substrate for
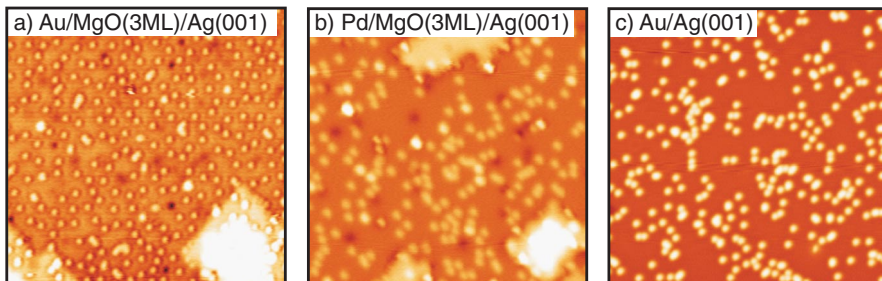

a) Au/MgO(3ML)/Ag(001)   b) Pd/MgO(3ML)/Ag(001)   c) Au/Ag(001)

FIG. 1 (color online). STM images (30 nm × 30 nm) of (a) Au atoms adsorbed on 3 ML thin MgO films ($\theta = 2.9\%$ ML Au, $V_S = +0.5$ V, $I_T = 11$ pA); (b) Pd atoms adsorbed on 3 ML thin MgO films ($\theta = 2.3\%$ ML Pd, $V_S = +0.2$ V, $I_T = 13$ pA); (c) Au atoms adsorbed on bare Ag(001) ($\theta = 2.9\%$ ML Au, $V_S = +0.1$ V, $I_T = 100$ pA).
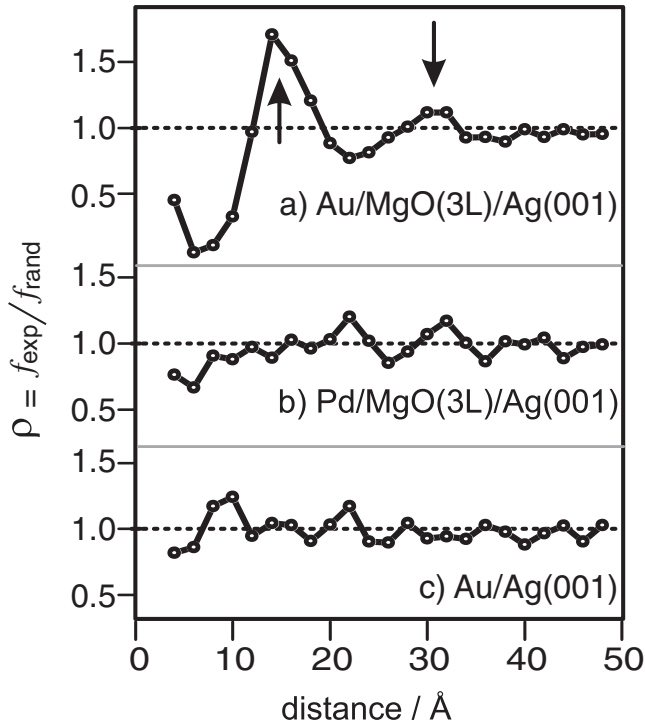
FIG. 2. Normalized radial pair distribution function $\rho = f_{exp}(r)/f_{rand}(r)$ for pair distances up to $r = 50$ Å for (a) Au atoms adsorbed on MgO(3L)/Ag(001), (b) Pd atoms adsorbed on MgO(3L)/Ag(001), and (c) Au atoms adsorbed on bare Ag(001). $\rho = 1$ corresponds to random site occupation.

this effect [24]. Two-dimensional ordering was found for Au atoms on a thin FeO(111) film on Pt(111). In this case, the ordering results from an inhomogeneous surface potential induced by a Moiré superlattice [25]. However, neither of the two effects can account for the ordering of Au atoms on the thin MgO films.

In a recent theoretical study it has been shown that Au atoms adsorbed on a thin MgO film are charged, in contrast to the situation found for unsupported MgO [11]. This process requires on the one hand a work function reduction of the metal substrate by the thin oxide film, and on the other hand a high electron affinity of the adsorbed metal atoms. For thin MgO films supported by Ag(001) or Mo(001) a reduction of the work function was found experimentally as well as theoretically [26–29]. In case of Au atoms adsorbed on supported MgO, DFT calculations reveal a charge transfer towards the Au atoms for MgO film thicknesses of 1–5 ML [11,13]. In these calculations the unoccupied part of the Au 6s level shifts below the Fermi energy. The stabilization of this state is strongly driven by the image charge in the Ag substrate and strong structural modifications of the adsorption site on the MgO surface. With increasing MgO film thickness these effects diminish in importance and Au atoms on bulk MgO or thick films are neutral as shown experimentally for a 20 ML thick film on Mo(100) [14]. As compared to Au, Pd has a much lower electron affinity, thus, DFT calculations

show the Pd 5s level to remain above the Fermi energy—meaning the Pd atoms remain neutral even on ultimately thin MgO films of 1 ML thickness [11]. Based on these theoretical considerations the experimentally observed two-dimensional order of Au atoms adsorbed on a 3 ML thin MgO film [Fig. 1(a)] can be explained by the repulsive interactions between partially negatively charged Au atoms. It is important to mention at this point that the adsorbed gold atoms need to diffuse on the surface in order to arrange in the ordered fashion observed. We ascribe this to transient diffusion due to the low diffusion barrier of the charged gold atoms on the surface of the thin MgO film ($E_d = 0.08$ eV [30]) that can be overcome by the energy released during deposition. The Pd atoms remain neutral when adsorbed on the thin MgO film and, according to diffusion-limited deposition at the given experimental conditions, are randomly distributed on the surface. This result implies that for Pd adsorption the 3 ML thin MgO film resembles essentially the properties of bulk MgO(100), which is consistent with calculated binding energies for Pd on unsupported and supported MgO [30], as well as with earlier STM/STS data, which showed that a 3 layer thin MgO film develops a band gap comparable to the one of bulk MgO [26].

Is there further evidence that can be acquired from the STM experiments for the interpretation that Au atoms are charged, whereas Pd atoms remain neutral when adsorbed on a 3 ML thin MgO film? To this end we compare the experimental STM signatures of single Au and Pd atoms with simulated ones applying the Tersoff-Hamann approximation [31] on the electronic structure derived by DFT calculations, where Au atoms are charged and Pd atoms are neutral, respectively (Fig. 3). In experiment, the Au atoms are imaged as protrusions surrounded by a depression [Figs. 3(a) and 3(b)], whereas Pd appears as a diffuse protrusion only [Figs. 3(d) and 3(e)]. Both the size of the
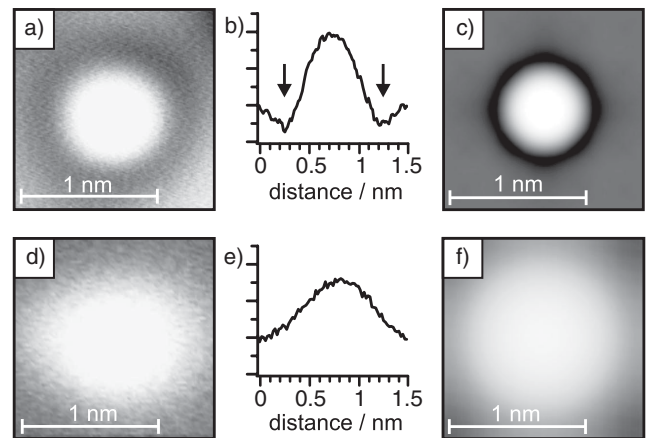

FIG. 3. Experimental STM images and height profiles, and corresponding simulated STM images of single Au (a–c) and Pd (d–f) atoms on the surface of 3 ML MgO/Ag(001), respectively. The bias voltage in the experimental and simulated STM images is $V_S = +0.5$ V.

atoms as well as the depression in case of the Au atom is very well reproduced by the simulated STM images [Figs. 3(c) and 3(f), respectively] corroborating our assignment of the different charge states of the respective metal atoms. This is further shown by the fact that the ''sombrerolike'' shape in the STM image of the Au atom is not present for a neutral Au adsorbate. Charged gold is stabilized by a strong polaronic distortion of the oxide substrate [13,30], but if the MgO geometry is fixed to that of truncated bulk the calculation converges to a neutral Au^0 adsorbate whose STM image (not shown here for brevity) does not exhibit the depression of Fig. 3(a), and is hardly distinguishable from that of Pd [Fig. 3(d)]. A characteristic depression around Au atoms was recently observed for Au on 2 ML thin NaCl films [32]. However, in the case of Au/NaCl(100)/Cu(111) the atoms were neutral directly after evaporation. Charging of the atoms was induced by a voltage pulse applied between sample and STM tip. In contrast to these experiments the Au atoms observed on the thin MgO film show the ringlike depression immediately after deposition indicating that charging of Au occurs in the course of the adsorption process.

It was proposed by theory that similar charging effects as for gold may occur for other adsorbates on thin MgO films. For example, from DFT calculations a positive charging of potassium atoms when adsorbed on a 2 ML thin MgO film supported on Ag(001) was found [13]. Nitrites (NO_2^-) are formed due to charge abstraction from the oxide upon adsorption of NO_2 on supported MgO films in contrast to adsorption on unsupported MgO, where NO_2 stays essentially neutral [33]. These examples illustrate that the interaction of adsorbates exhibiting particular electronic properties with supported MgO thin films can give rise to a modification of the properties of adsorbed metals or molecules and can thus be used to tune the chemical activity of these systems.

In conclusion, the results presented in this study provide the first experimental evidence for the presence of charged Au atoms on a thin, Ag(001)-supported MgO layer as proposed by calculations [11], in contrast to Au atoms on thick MgO films, which were proven to be neutral [14]. No charging effect is evident from our STM data for Pd atoms. As a consequence, while the Au atoms exhibit two-dimensional ordering due to repulsive interactions between the charged entities, no ordering is present for Pd. The observation of the charging of Au adsorbed on a thin MgO film is a direct consequence of the work function reduction of the metal substrate by the thin film, and depends critically on the electron affinity of the adsorbed metal. The experimental verification of this hypothesis associates credibility to the proposal to use combinations of various thin oxide films and deposited metals to tune surface reactivity.

The authors are indebted to E. D. L. Rienks for very helpful discussions. This work has been supported by the

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