

Gold Supported on Thin Oxide Films: From Single Atoms to Nanoparticles

THOMAS RISSE, SHAMIL SHAIKHUTDINOV, NIKLAS NILIUS,
MARTIN STERRER, AND HANS-JOACHIM FREUND*

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

RECEIVED ON MARCH 6, 2008

CON SPECTUS

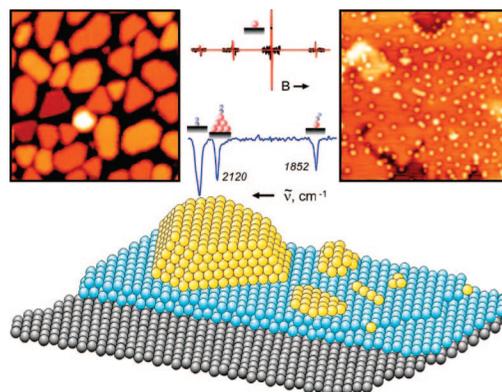
Historically, people have prized gold for its beauty and the durability that resulted from its chemical inertness. However, even the ancient Romans had noted that finely dispersed gold can give rise to particular optical phenomena. A decade ago, researchers found that highly dispersed gold supported on oxides exhibits high chemical activity in a number of reactions. These chemical and optical properties have recently prompted considerable interest in applications of nanodispersed gold.

Despite their broad use, a microscopic understanding of these gold–metal oxide systems lags behind their application. Numerous studies are currently underway to understand why supported nanometer-sized gold particles show catalytic activity and to explore possible applications of their optical properties in photonics and biology.

This Account focuses on a microscopic understanding of the gold–substrate interaction and its impact on the properties of the adsorbed gold. Our strategy uses model systems in which gold atoms and clusters are supported on well-ordered thin oxide films grown on metal single crystals. As a result, we can investigate the systems with the rigor of modern surface science techniques while incorporating some of the complexity found in technological applications.

We use a variety of different experimental methods, namely, scanning probe techniques (scanning tunneling microscopy and spectroscopy, STM and STS), as well as infrared (IR), temperature-programmed desorption (TPD), and electron paramagnetic resonance (EPR) spectroscopy, to evaluate these interactions and combine these results with theoretical calculations. We examined the properties of supported gold with increasing complexity starting from single gold atoms to one- and two-dimensional clusters and three-dimensional particles. These investigations show that the binding of gold on oxide surfaces depends on the properties of the oxide, which leads to different electronic properties of the Au deposits. Changes in the electronic structure, namely, the charge state of Au atoms and clusters, can be induced by surface defects such as color centers.

Interestingly, the film thickness can also serve as a parameter to alter the properties of Au. Thin MgO films (two to three monolayer thickness) stabilize negatively charged Au atoms and two-dimensional Au particles. In three dimensions, the properties of Au particles bigger than 2–3 nm in diameter are largely independent of the support. Smaller three-dimensional particles, however, showed differences based on the supporting oxide. Presumably, the oxide support stabilizes particular atomic configurations, charge states, or electronic properties of the ultras-small Au aggregates, which are in turn responsible for this distinct chemical behavior.



Introduction

Gold is known for durability and beauty. The reason is, of course, its inertness in chemical reactions. Nevertheless, it has been recognized since

Roman times that finely dispersed gold gives rise to optical phenomena (red “gold” glass).¹ About a decade ago, it was found that highly dispersed gold supported on oxides exhibits high chemical

activity in an increasing number of chemical reactions.^{2,3} The properties of nanodispersed gold have stimulated a huge number of studies in catalysis, photonics, and biology. Despite the enormous interest and enhanced activities worldwide, the details of the electronic properties of the small gold particles as they interact with the supports have not been revealed at the atomic scale. This renders careful model studies a necessity. In particular, the studies of metal particles supported on planar oxide substrates under well-controlled conditions were envisioned to provide fundamental insights into the relationships between the atomic structure and the physical and chemical properties of supported gold clusters (see, for instance refs 4–6). In this Account, we will go beyond previous Accounts by adding aspects of the structure–property relationships of atoms and particles as well as the influence of the support. This Account focuses on recent studies in our group and neglects various aspects such as Au on bulk oxides. For those aspects, the interested reader is referred to the literature.^{4,7}

It is well-known that gold exhibits a relatively high electronegativity and high ionization potential, which renders gold a poor electron donor. As a result, gold interacts weakly with many oxides. Thus, the substrate temperature during physical vapor deposition (PVD) of gold may alter the nucleation and growth processes since the Au adatoms may escape from defect sites at higher temperatures, migrate on the surface, and hence agglomerate. Also, the size and the shape of the gold aggregates depend on the temperature and can be metastable once formed at low temperatures. Not surprisingly, oxygen vacancies were found to play an important role in the adsorption of gold on oxide surfaces.⁸ The nature of the oxygen vacancies depends on the charge state of the vacancy and the associated redistribution of charge in its surroundings which correlates to a first approximation with the ionicity of the oxide under consideration. Finally, in the case of the ultrathin oxide films, the metal substrate lying underneath the film may affect the properties of single Au adatoms and particles, thus leading to an adsorption behavior that depends on the oxide thickness.

In the following, we will discuss a number of examples for Au/oxide systems, which include single atoms, small clusters, two-dimensional islands, and three-dimensional nanoparticles on thin, well-ordered oxide films (as schematically shown in Figure 1) in order to demonstrate the complexity of the gold/oxide interaction. Thermal stability and effects of ambient gases on the structure of gold surface species have been also examined. We believe that the results provide us with a

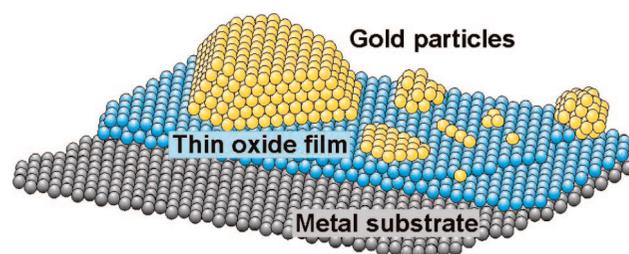


FIGURE 1. Schematic representation of the model systems used to study the size and shape, electronic structure, metal–support interactions, and adsorption properties of highly dispersed gold supported on oxide surfaces.

deeper understanding of the structure–property relationships of nanodispersed gold.

Single Supported Gold Atoms

Individual Au atoms interact rather weakly with stoichiometric oxide surfaces and as compared with Au–Au bonds. Thus, experiments aiming at an investigation of Au atoms require low temperature, as well as low coverage, to suppress the formation of Au aggregates. Within this Account, the properties of single Au atoms on different thin oxide films, namely, MgO(100)/Mo(001) or Ag(001), FeO(111)/Pt(111), SiO₂/Mo(112), and Al₁₀O₁₃/NiAl(110), will be discussed. The oxides range from highly ionic to more covalent ones, and it is instructive to compare these surfaces with respect to the changes in Au binding.

MgO, with its simple rock salt structure may be considered the prototype of an ionic oxide. There are well-established recipes to prepare single-crystalline MgO(001) on Mo(001)^{9–11} and Ag(001),^{12,13} which have been adopted here. Au atoms were prepared on a stoichiometric, ~20 monolayer (ML) thick MgO(001) film grown on Mo(001) by PVD of an equivalent of 0.01 ML Au at 35 K. The presence of single gold atoms on the surface was proven by electron paramagnetic resonance (EPR) spectroscopy. The EPR spectrum is characterized by a quartet of lines caused by the hyperfine interaction of the electron spin ($S = 1/2$) with the nuclear spin ($I(^{197}\text{Au}) = 3/2$; 100% natural abundance) of the neutral gold atoms (Figure 2a). A detailed analysis of angular-dependent EPR spectra allows a determination of the magnetic interaction parameters (g and hyperfine matrix) and proves the Au atoms to be located on terrace sites of the MgO(001) surface. This is in perfect agreement with low-temperature scanning tunneling microscopy (STM) results (Figure 2b).¹⁴ By analysis of the additional hyperfine interaction with O of an ¹⁷O enriched MgO films, the Au atoms were shown to adsorb on top of oxygen ions (Figure 2a) in agreement with theoretical predictions.^{15–17} Important information on the electronic structure is encoded in the hyperfine tensor components. Compared with that of Au

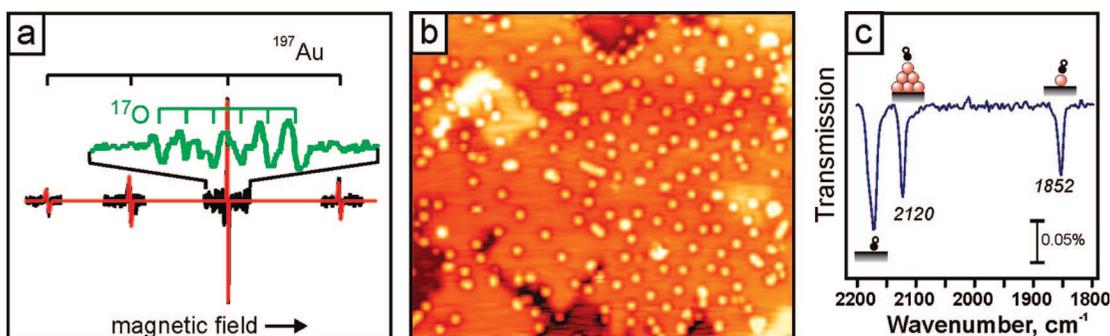


FIGURE 2. (a) Experimental and simulated EPR spectra of 0.01 ML Au atoms adsorbed on a 20 ML thick MgO(001) film on Mo(001). EPR spectrum of Au atoms on an ^{17}O enriched MgO film is shown in green. (b) STM image ($30 \times 25 \text{ nm}^2$) of Au atoms (0.035 ML) deposited at 8 K on ~ 8 ML thick MgO(001)/Ag(001) film. (c) IR spectrum of CO adsorbed on Au atoms and clusters on a MgO(001) film.

atoms in the gas phase, the isotropic part of the hyperfine interaction, associated with the spin density at the nucleus, is reduced by about 50%, pointing to a significant redistribution of electron density upon binding to the surface. There are different scenarios conceivable to rationalize this finding including a charge transfer onto the Au atom. DFT calculations showed, however, that this effect is due to a polarization of the singly occupied 6s orbital of neutral Au atoms away from the MgO surface.¹⁴

Infrared (IR) spectroscopy is often used to obtain information on the properties of metals employing simple probe molecules such as CO. This strategy was extensively applied to characterize supported gold catalysts (ref 7 and references therein). When this strategy was applied to the previously discussed system, the infrared spectra taken after saturating Au with CO result in two IR bands centered at 2120 and 1852 cm^{-1} (Figure 2c).¹⁸ The former signal can be assigned to CO adsorbed on small neutral Au clusters, whereas the latter one, red-shifted by 291 and 180 cm^{-1} compared with gas-phase CO and Au–CO complex,¹⁹ respectively, is associated with single Au atoms. The large red shift, indicating a significant charge transfer into the π^* -orbital of the CO, is usually interpreted as an indication for negatively charged Au atoms, which was proven (see above) not to be the case. A detailed theoretical analysis of this system reveals that the large red shift is caused by the largely polarized valence electron of the adsorbed Au atoms, which creates a $\text{Au}^{\delta+}\text{CO}^{\delta-}$ complex on the surface. This shows that particularly for atoms or very small clusters, probe molecules such as CO may fail to properly report on the properties of the underlying metal.¹⁸

The strongly polarized adsorption of Au atoms on top of oxygen anions of a MgO surface can be understood in a straightforward manner keeping in mind the large polarizability and the high electronegativity of Au atoms. The question arises whether these effects can be used to either manipulate the adsorption or, alternatively, probe properties of an

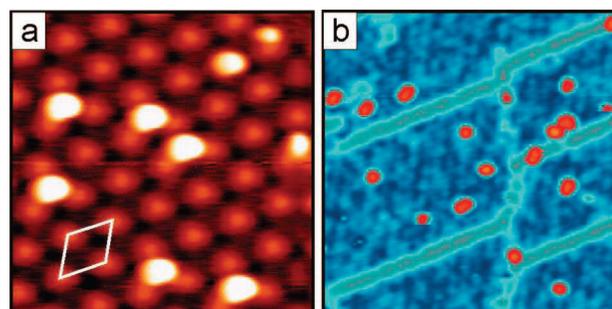


FIGURE 3. STM images of Au single atoms deposited on FeO(111)/Pt(111) (a) and $\text{Al}_{10}\text{O}_{13}/\text{NiAl}(110)$ (b) films at 5–10 K.^{23,29} (image sizes (a) $15 \times 15 \text{ nm}^2$ (b) and $30 \times 30 \text{ nm}^2$). The Moiré unit cell with a $\sim 25 \text{ \AA}$ lattice constant is indicated in panel a.

oxide surface. To this end polar oxide surfaces, characterized by a divergence of the Madelung potential in case of thicker films, are particularly well suited. The Madelung instability occurs if charged planes of ions alternate perpendicular to the surface. One of the main questions is the mechanism by which the film reduces its electrostatic potential. As an example, an FeO(111) film grown on Pt(111) will be discussed here.^{20–22} This film, which consists of one Fe layer in contact with the Pt substrate and a terminating oxygen layer, forms a Moiré pattern with a periodicity of $\sim 25 \text{ \AA}$ due to the lattice mismatch between FeO(111) and Pt(111). Deposition of Au atoms onto this surface at low temperature (5 K) results in the formation of a well-ordered superstructure of Au atoms, which maps the Moiré pattern of the underlying surface.²³ The registry analysis of the single Au atoms within the Moiré unit cell (see rhomb in Figure 3a) revealed that Au adsorbs preferentially on the so-called hcp domain, which exhibits the largest dipole moment. The latter is determined by the distance between the $\text{Fe}^{\delta+}$ and $\text{O}^{\delta-}$ layers, which is in turn governed by the registry with the underlying Pt substrate.²⁴ The adsorption of gold atoms on the sites with the largest dipole moment results in the largest polarization of the adatoms in the dipole field of the oxide and therefore strengthens the gold–oxide bond.

The Au adatoms appear in the STM images as large protrusions (Figure 2a).²³ This rather large size has an electronic origin and is basically due to the extension of the Au 6s electron wave function above the surface plane. Additional interesting information on the electronic properties of the Au atoms can be gathered using tunneling spectroscopy (TS). The spectra revealed a Au related state ~ 0.5 eV above the Fermi level.²³ This unoccupied state is attributed to the Au 6s orbital, which suggests positive charging of the adatom in agreement with theoretical predictions. Such an unusual charge state of Au adatoms is owed to the high Pt(111) workfunction that is further increased by the polar FeO(111) film and inhibits charge transfer into the Au adatoms.²⁵

The situation is considerably different for Au atoms on a thin alumina film grown on NiAl(110).²⁶ The film consists of two O–Al layers (O_s – Al_s – O_i – Al_i –NiAl...) with a rather complex structure and exhibits an overall $Al_{10}O_{13}$ stoichiometry.^{26,27} Single Au atoms were deposited and imaged by STM at low temperature (10 K) (see Figure 3b).^{28,29} In contrast to the FeO case, the tunneling spectra of the Au atoms lack an unoccupied state of Au 6s character. Also the appearance of Au adatoms as faint protrusions in STM images, taken at positive bias, indicates the absence of unoccupied states below the alumina conduction band and therefore suggests a completely filled Au 6s orbital located below the Fermi level. The presence of a negative excess charge in the Au is further corroborated by DFT calculations that also provide a detailed picture for the binding characteristics.²⁹ The Au atoms adsorb on top of Al_s sites, which are located above Al in the topmost layer of the NiAl(110) substrate. The charge transfer results from a Au-induced rupture of an Al_s – O_i bond in the alumina film. The Au 6s hybridizes with the 3s orbital of the Al_s and abstracts an electron to form a negatively charged Au atom. The coordinatively unsaturated interface oxygen restores its preferred valence by a new bond to the Al atom of the NiAl substrate. Chemically speaking the Au atoms oxidize the NiAl surface.

For more covalent oxides, the interaction with Au due to polarization will decrease, and Au is expected to bind only weakly as long as the oxide surface is chemically inert (see alumina/NiAl(110)). However, as seen from the Au/FeO(111) surface discussed above, additional effects may complicate such a simple picture. A system that follows this expectation almost perfectly is a thin single-crystalline silica film grown on Mo(112).³⁰ The film consists of a monolayer network of corner-sharing $[SiO_4]$ tetrahedra with one oxygen atom bonded to the Mo substrate.³¹ The interaction of Au with this silica surface is found to be very weak. Even at 10 K, Au atoms dif-

fuse to the antiphase domain boundaries present in the film, where stronger binding becomes feasible. It is worth noting that this behavior is different for other metal atoms, which may penetrate the honeycomb-like film as theoretically predicted for Pd and recently verified by STM.^{32–34}

One can take these results a step further and ask the question whether it is possible to manipulate this interaction by changing the properties of the oxide. This is indeed possible and was demonstrated using MgO(001) films as prototype examples. One way to alter the properties of adsorbed species is to create new, preferably reactive centers on the surface. A class of centers that is particularly interesting with respect to oxides is oxygen vacancies also known as color centers. A combination of STM/STS and EPR spectroscopy was employed to prove the presence of intentionally created oxygen vacancies located on edges and corners of the MgO islands.^{13,35} It is possible to show that Au atoms become negatively charged on thick MgO films upon binding to oxygen vacancies, as verified by a combination of IR spectroscopy and theoretical calculations.³⁶ Another strategy to alter the properties of Au atoms deposited on thin MgO films is to reduce the thickness of the MgO films. In contrast to the “thick” MgO films, DFT calculations predicted a charge transfer from the metal substrate onto gold atoms when the gold atoms are deposited onto the thin, 2–3 ML films.³⁷ The deposition of MgO onto the metal substrate reduces the work function of the system. In turn, the unoccupied part of the Au 6s level is shifted below the Fermi energy. Low-temperature STM experiments of Au atoms on 3 ML thin MgO(001) films provided convincing evidence for this charging effect. First, an ordered arrangement of atoms is observed reflecting the repulsive interaction as expected for charged species. Second, the preferred adsorption site being the oxygen on top sites for bulk-like MgO changes in favor of the Mg sites.^{38,39} This is in close correspondence to the behavior on the thin alumina film discussed above, where Au adsorbs on top of Al cations. It is worth noting that this effect is a peculiarity of Au while other metals with lower electron affinities such as Pd behave as expected for bulk oxides, that is, do not exhibit any charge transfer.

One- and Two-Dimensional Structures

From a thermodynamic point of view Au tends to form three-dimensional (3D) particles on oxide surfaces owing to the lower surface energies of oxides compared with metals. However, under kinetically limited growth conditions, structures with lower dimensionality can be prepared as well. Their stability strongly depends on the system under study and might

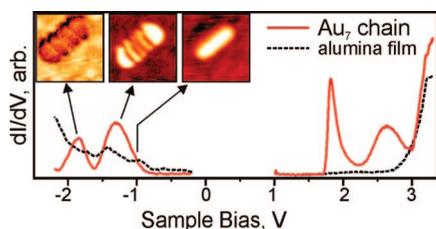


FIGURE 4. Tunneling spectra of an Au₇ chain on alumina/NiAl(110).²⁹ The states at -1.8 , -1.3 , and $+2.7$ V belong to a set of $s-d_{z^2}$ -like quantum well states, whereas the states at $+1.8$ and 3.5 V belong to a set of p -like states. The inset shows dI/dV images of two highest occupied states as well as a topographic image of the Au₇ chain.

require low temperatures as seen in the previous section. However, certain substrates have a sufficiently enhanced interaction to stabilize low-dimensional structures even at higher temperatures. The reduced dimensionality is often associated with peculiar properties, and the following section will discuss some examples focusing on the properties of such aggregates.

When Au atoms are deposited on oxide films even at low temperatures, it is expected that gold clustering may also occur. It is, however, surprising to see the formation of linear Au aggregates of up to seven atoms upon deposition at 10 K on alumina films (see also Figure 4).^{28,29} The Au chains are exclusively aligned with the [001] direction of NiAl(110), despite the 3-fold symmetry of the oxide layer. This finding indicates that the metal substrate is involved in the interaction of the Au atoms with the thin alumina film. The Au chains exhibit an interatomic distance of about 2.5 Å, which is only slightly larger than the Au–Au bond in Au₂ cluster in the gas phase (2.47 Å).⁴⁰ As discussed previously, strong Au binding takes place to those Al_s sites, which are located directly above an Al atom in NiAl(110). The incommensurate structure of alumina on NiAl(110) renders such configuration rather unlikely on the surface. However, the Al_s ions next to a favorable site often provide a similar Au binding potential, because they are located above one and the same [001] oriented Al row in NiAl(110) and thus enable the same interaction mechanism. Consequently, close-packed Au chains of 10–22 Å in length are formed on the alumina film surface above Al rows of the support, which are limited in length only by the slight misalignment between the Al_s orientation and the NiAl[100] direction. For Au chains of known size, their charge state can be inferred from the electron filling of quantum well states developing in the 1D potential well, as determined by STS and corroborated by DFT calculations. The analysis reveals that the Au₂–Au₄ chains carry two while the longer chains (Au₅–Au₇) carry three negative charges.²⁹

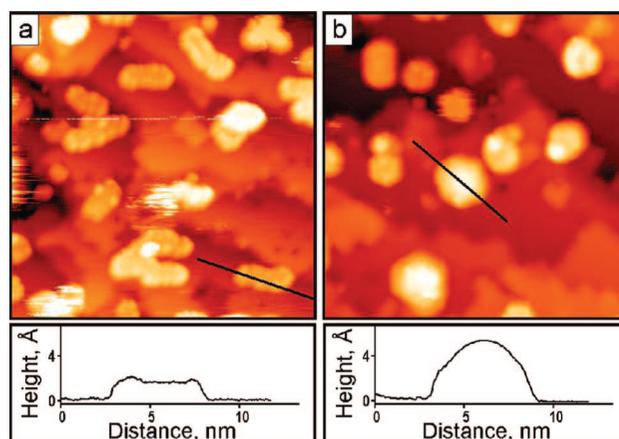


FIGURE 5. Room-temperature STM images (30×30 nm², $T = 5$ K) of Au deposited at 5 K and subsequently annealed to 300 K on a (a) 3 ML MgO(001) and (b) 8 ML MgO(001) films.

These linear Au chains are stable only at relatively low temperatures (<77 K). Also, for Au on thin (2–3 ML) MgO films, DFT calculations predicted a stabilization of negatively charged 2D particles as opposed to neutral 3D ones on bulk-like MgO.⁴¹ This stabilization is driven by a combination of polaronic distortions of the MgO film and image charge effects as discussed in the previous section for Au atoms. This prediction was verified in a recent STM study where heating of Au deposited at 5 K onto 3 ML MgO(001)/Ag(001) to 300 K results in 2D Au islands (Figure 5a), while the same experiment on a thick (8 ML) MgO film favors the formation of 3D nanoparticles (Figure 5b).³⁸

A similar behavior is found for Au deposited on the FeO(111)/Pt(111) at higher temperatures. Deposition of below 0.1 ML Au at 120 K and subsequent annealing to 300 K results in 2D particles, which are stable even after annealing to 500 K.⁴² It seems plausible that the interaction of Au with the surface dipole stabilizes the Au/FeO interface and thus the 2D structures. Interestingly, adsorption of CO onto these 2D gold islands gives rise to IR spectra, as well as desorption temperatures in temperature-programmed desorption (TPD) spectra, that are comparable to those found for large Au particles.^{42,43} This suggests that quantum size effects may not govern reactivity of Au in the CO oxidation reaction as previously inferred for Au on TiO₂(110) by tunneling spectroscopy.⁴⁴

Gold Nanoparticles: Support Effects

Gold deposition at or heating to 300 K results in the formation of 3D particles on all supports discussed here. The properties of nanoparticles exhibiting a particle size >2 nm as probed by STM, IR, and TPD of CO are basically independent of the substrate: gold forms well-faceted particles with stretch-

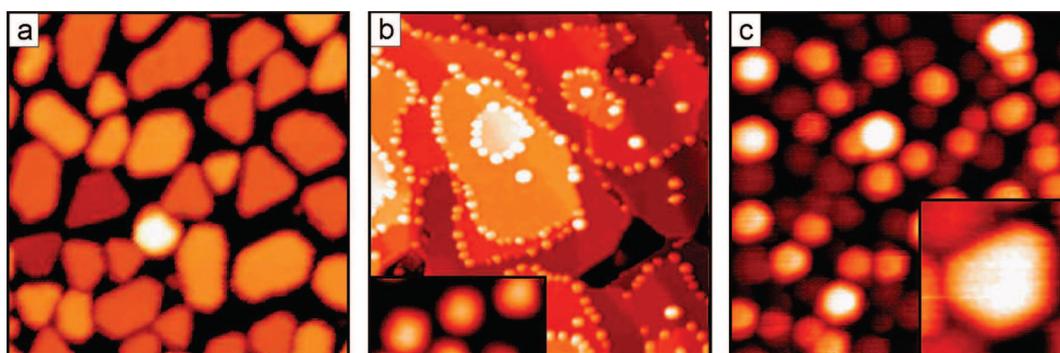


FIGURE 6. STM images of (a) Au/Al₁₀O₁₃/NiAl(110) (50 × 50 nm²), (b) Au/CeO₂(111) (120 × 120 nm²), and (c) Au/Fe₃O₄(111) (40 × 40 nm²) surfaces prepared at 300 K. Insets showed magnified parts of the images.

ing frequency of CO ($\tilde{\nu}_{\text{CO}}$) around 2110 cm⁻¹ and two CO desorption peaks at temperatures (T_{des}) in the range of 130–180 K. A variation of $\tilde{\nu}_{\text{CO}}$ and T_{des} is usually observed only when smaller particles are formed that bind CO more strongly. A typical example is Au deposited at 300 K on the alumina film. The Au clusters are 3D independent of coverage. Larger particles form well-faceted islands with a (111) oriented top facet (Figure 6a). If the clusters size is smaller than about 2 nm, CO molecules get more strongly bound and the desorption extends up to ~250 K.⁴⁵

Besides this universal behavior of larger particles and stronger CO binding on smaller clusters, there are, however, considerable differences in Au nucleation and hence cluster distribution observed for Au clusters that are related to either the chemical nature of the support or the presence of point defects (inherently present or artificially created).

Well-faceted Au particles on the alumina/NiAl(110) surface are statistically distributed with no preference for the network of dislocation lines, which are preferential nucleation sites for electropositive metals such as Pd.⁴⁶ In contrast, Au crystallites prepared at 300 K on CeO₂(111) films grown on Ru(0001)⁴⁷ are preferentially nucleated at step edges as long as the number of point defects is small (Figure 6b). Compared with those on the alumina surface, the particles are more resistant toward sintering and do not alter after annealing to 500 K. Nucleation on terrace sites takes place only after saturation of the step sites with particles of a certain size, which suggests a self-limiting growth mechanism in this case. The nucleation behavior can be modified by reduction of the surface upon high-temperature annealing, which results in point defects on the CeO₂(111) terraces. The point defects serve as nucleation sites for Au; hence, cluster formation is observed on the terrace even for small coverage. Surface vacancies are presumably also responsible for the broad size distribution of 3D Au particles grown on Fe₃O₄(111)/Pt(111)⁴⁸ after deposition at 300 K.⁴⁵ Heating of the system induces Ostwald rip-

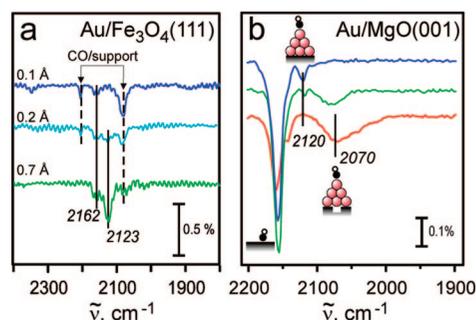


FIGURE 7. IR spectra of CO adsorbed on (a) Au particles increasing size on Fe₃O₄. b) Au on MgO(001) films. The upper trace shows Au clusters on stoichiometric MgO films; lower traces show Au clusters deposited on color centers.

ening, and well-faceted, (111)-oriented particles are found (Figure 6c). For small Au particles deposited on Fe₃O₄(111) at 90 K, an additional CO band at 2165 is observed (Figure 7a). The position of the signal suggests the formation of cationic Au^{+δ} species on these supports. It is tempting to correlate their occurrence with the presence of point defects on the surfaces. However, one has to keep in mind that point defects on highly ionic oxides, such as MgO, produce negatively charged Au particles exhibiting a red shift of the CO stretching band by 40–100 cm⁻¹ depending on particle size (Figure 7b).³⁶

Apart from a microscopic characterization of the interaction between gold and oxide surfaces discussed in detail above, the group has also worked on more application-oriented facets of these systems. For example, optical properties of Au particles were investigated on the single-particle level focusing on the impact of the substrate on these properties as well as the ability to tune them. Another aspect that is particularly important with respect to catalytic applications relates to environmental effects, that is, the influence of catalytically relevant gas atmospheres on the stability and mobility of gold species on oxide surfaces. These topics are beyond the scope of this Account, and the reader is referred to the corresponding literature.^{49–53}

Concluding Remarks

Numerous experimental and theoretical studies aimed at a better understanding of the unique properties of gold in the nanometer size regime are currently being performed. Our studies demonstrate that small Au aggregates ranging from single atoms to nanoparticles exhibit electronic, optical (not covered herein), and chemical characteristics different from those of bulk gold. It was shown that these characteristics can be tuned using the thickness of the oxide film as control parameter. The size-dependent changes in the electronic structure of gold may give rise to its unique catalytic properties. It seems plausible that the role of the oxide support is to stabilize particular atomic configurations, charge states, or electronic properties of the ultrasmall Au aggregates, which are in turn responsible for a distinct chemical behavior.

The authors thank H. M. Benia, M. Heyde, M. Kulawik, C. Lemire, J.-L. Lu, R. Meyer, E. Rienks, H.-P. Rust, D. Starr, S. Ulrich, and M. Yulikov. We are indebted to Joachim Sauer (Berlin) and Gianfranco Pacchioni (Milan), as well as their groups, for very fruitful collaborations. The authors also acknowledge support from the Cluster of Excellence "Unifying Concepts in Catalysis".

BIOGRAPHICAL INFORMATION

Thomas Risse has been a group leader in the Department of Chemical Physics at the Fritz-Haber-Institute since 1997 after completing his doctorate in Physical Chemistry at Bochum University. From 1999 to 2000, he spent a year at UCLA working with Wayne Hubbell. His research interest is focused on the application of electron spin resonance spectroscopy to well-defined surfaces. The systems investigated range from paramagnetic centers on surfaces to site-directed spin labeling of adsorbed proteins.

Shamil Shaikhutdinov has received his Ph.D. (1986) in Physics from the Moscow Institute of Physics and Technology. Then he joined the group of Prof. K. Zamaraev at the Borekov Institute of Catalysis (Novosibirsk) working on the application of surface science techniques to catalytic systems. In 1998, he became a postdoctoral fellow and in 2004 a group leader at the Fritz-Haber-Institute. His research interest is focused on an understanding of structure–reactivity relationships in heterogeneous catalysis.

Niklas Nilius studied physics and received his Ph.D. in the group of H.-J. Freund investigating the optical properties of single metal particles by Photon-STM. Between 2002 and 2003, he worked as a postdoctoral fellow with Wilson Ho on the properties of atomic chains artificially assembled on metal surfaces. His current research is focused on the adsorption characteristic of thin oxide films and on local optical properties of oxide surfaces.

Martin Sterrer has received his doctorate in Physical Chemistry from Vienna University of Technology in 2003. He joined the Department of Chemical Physics at the Fritz-Haber-Institute as a postdoctoral fellow in 2003 and became a group leader there in

2006. In that year, he spent 4 months at the FOM institute for Atomic and Molecular Physics (AMOLF) in Amsterdam, The Netherlands, working with Mischa Bonn. His current research is focused on the interfacial properties of oxide surfaces and oxide-supported metal clusters at elevated pressure as well as liquid environments.

Hans-Joachim Freund studied physics and chemistry at the University of Cologne where he received his Ph.D. in 1978 and his habilitation in 1983. Between 1979 and 1981, he worked in the Physics Department at the University of Pennsylvania as a postdoctoral fellow. In 1983, he became Associate Professor at Erlangen University and in 1987 Professor at Bochum University, and in 1995, he accepted a position as scientific member and director of the Department of Chemical Physics at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin. He serves as Honorary Professor of four universities. He received several awards including the Leibniz Award (DE), the ACS Somorjai Award (US), and the Centenary Medal (UK). He is a member of several academies, scientific societies, and advisory boards of scientific journals and is a founding member of the Scientific Council of the European Research Council. He has published more than 500 scientific papers and given more than 520 invited talks.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: freund@fhi-berlin.mpg.de.

REFERENCES

- Kreibig, U.; Vollmer, W. *Optical Properties of Metal Clusters*; Springer Series in Material Science; Springer: Berlin, 1995; Vol. 25.
- Haruta, M. When Gold Is Not Noble: Catalysis by Nanoparticles. *Chem. Rec.* **2003**, *3*, 75–87.
- Bond, G. C.; Thompson, D. T.; Louis, C. *Catalysis by Gold*; Catalytic Science Series; Imperial College Press: London, 2006; Vol. 6.
- Chen, M.; Goodman, D. W. Catalytically Active Gold: From Nanoparticles to Ultrathin Films. *Acc. Chem. Res.* **2006**, *39*, 739–746.
- Cosandey, F.; Madey, T. E. Growth, Morphology, Interfacial Effects, and Catalytic Properties of Au on TiO₂. *Surf. Rev. Lett.* **2001**, *8*, 73–93.
- Freund, H.-J. Clusters and Islands on Oxides: From Catalysis via Electronics and Magnetism to Optics. *Surf. Sci.* **2002**, *500*, 271–299.
- Meyer, R.; Lemire, C.; Shaikhutdinov, S. K.; Freund, H. J. Surface Chemistry of Catalysis by Gold. *Gold Bull.* **2004**, *37*, 72–124.
- Wahlström, E.; Lopez, N.; Schaub, R.; Thøstrup, P.; Rønnow, A.; Africh, C.; Lægsgaard, E.; Nørskov, J. K.; Besenbacher, F. Bonding of Gold Nanoclusters to Oxygen Vacancies on Rutile TiO₂(110). *Phys. Rev. Lett.* **2003**, *90*, 026101.
- Wu, M. C.; Corneille, J. S.; He, J. W.; Estrada, C. A.; Goodman, D. W. Preparation, Characterization, and Chemical-Properties of Ultrathin MgO Films on Mo(100). *J. Vac. Sci. Technol. A* **1992**, *10*, 1467–1471.
- Sterrer, M.; Risse, T.; Freund, H.-J. Low Temperature Infrared Spectra of CO Adsorbed on the Surface of MgO(001) Thin Films. *Surf. Sci.* **2005**, *596*, 222–228.
- Benedetti, S.; Benia, H. M.; Nilius, N.; Valeri, S.; Freund, H. J. Morphology and optical properties of MgO thin films on Mo(001). *Chem. Phys. Lett.* **2006**, *430*, 330–335.
- Wollschläger, J.; Viernow, J.; Tegenkamp, C.; Erdös, D.; Schröder, K. M.; Pfnür, H. Stoichiometry and Morphology of MgO Films Grown Reactively on Ag(100). *Appl. Surf. Sci.* **1999**, *142*, 129–134.
- Sterrer, M.; Heyde, M.; Novicki, M.; Nilius, N.; Risse, T.; Rust, H. P.; Pacchioni, G.; Freund, H.-J. Identification of Color Centers on MgO(001) Thin Films with Scanning Tunneling Microscopy. *J. Phys. Chem. B* **2006**, *110*, 46–49.
- Yulikov, M.; Sterrer, M.; Heyde, M.; Rust, H. P.; Risse, T.; Freund, H.-J.; Pacchioni, G.; Scagnelli, A. Binding of single gold atoms on thin MgO(001) films. *Phys. Rev. Lett.* **2006**, *96*, 146804.
- Yudanov, I.; Pacchioni, G.; Neyman, K.; Röscher, N. Systematic Density Functional Study of the Adsorption of Transition Metal Atoms on the MgO(001) Surface. *J. Phys. Chem. B* **1997**, *101*, 2786–2792.

- 16 Del Vitto, A.; Pacchioni, G.; Delbecq, F. O.; Sautet, P. Au Atoms and Dimers on the MgO(100) Surface: A DFT Study of Nucleation at Defects. *J. Phys. Chem. B* **2005**, *109*, 8040–8048.
- 17 Barcaro, G.; Fortunelli, A. The Interaction of Coinage Metal Clusters with the MgO(100) Surface. *J. Chem. Theory Comput.* **2005**, *1*, 972–985.
- 18 Sterrer, M.; Yulikov, M.; Risse, T.; Freund, H.-J.; Carrasco, J.; Illas, F.; Di Valentin, C.; Giordano, L.; Pacchioni, G. When the Reporter Induces the Effect: Unusual IR Spectra of CO on Au_n/MgO(001)/Mo(001). *Angew. Chem., Int. Ed.* **2006**, *45*, 2633–2635.
- 19 Jiang, L.; Xu, Q. Reactions of Gold Atoms and Small Clusters with CO: Infrared Spectroscopic and Theoretical Characterization of Au_nCO ($n = 1-5$) and Au_n(CO)₂ ($n = 1, 2$) in Solid Argon. *J. Phys. Chem. A* **2005**, *109*, 1026–1032.
- 20 Vurens, G. H.; Salmeron, M.; Somorjai, G. A. Structure, Composition and Chemisorption Studies of Thin Ordered Iron Oxide Films on Platinum(111). *Surf. Sci.* **1988**, *201*, 129–144.
- 21 Kim, Y. J.; Westphal, C.; Ynzunza, R. X.; Galloway, H. C.; Salmeron, M.; Van Hove, M. A.; Fadley, C. S. Interlayer Interactions in Epitaxial Oxide Growth: FeO on Pt(111). *Phys. Rev. B* **1997**, *55*, R13448–R13551.
- 22 Ritter, M.; Ranke, W.; Weiss, W. Growth and Structure of Ultrathin FeO Films on Pt(111) Studied by STM and LEED. *Phys. Rev. B* **1998**, *57*, 7240–7251.
- 23 Nilius, N.; Rienks, E. D. L.; Rust, H. P.; Freund, H. J. Self-Organization of Gold Atoms on a Polar FeO(111) Surface. *Phys. Rev. Lett.* **2005**, *95*, 066101.
- 24 Rienks, E. D. L.; Nilius, N.; Rust, H. P.; Freund, H. J. Surface Potential of a Polar Oxide Film: FeO on Pt(111). *Phys. Rev. B* **2005**, *71*, 241404.
- 25 Giordano, L.; Pacchioni, G.; Goniakowski, J.; Nilius, N.; Rienks, E. D. L.; Freund, H.-J. Interplay between Structural, Magnetic, and Electronic Properties in a FeO/Pt(111) Ultrathin Film. *Phys. Rev. B* **2007**, *76*, 075416.
- 26 Jaeger, R. M.; Kuhlbeck, H.; Freund, H.-J.; Wuttig, M.; Hoffmann, W.; Franchy, R.; Ibach, H. Formation of well-ordered aluminium oxide overlayer by oxidation of NiAl(110). *Surf. Sci.* **1991**, *259*, 235–252.
- 27 Kresse, G.; Schmid, M.; Napetschnig, E.; Shishkin, M.; Köhler, L.; Varga, P. Structure of the Ultrathin Aluminum Oxide Film on NiAl(110). *Science* **2005**, *308*, 1440–1442.
- 28 Kulawik, M.; Nilius, N.; Freund, H. J. Influence of the Metal Substrate on the Adsorption Properties of Thin Oxide Layers: Au Atoms on a Thin Alumina Film on NiAl(110). *Phys. Rev. Lett.* **2006**, *96*, 036103.
- 29 Nilius, N.; Ganduglia-Pirovano, M. V.; Brazdova, V.; Kulawik, M.; Sauer, J.; Freund, H. J. Counting Electrons Transferred through a Thin Alumina Film into Au Chains. *Phys. Rev. Lett.* **2008**, *100*, 096802.
- 30 Schroeder, T.; Adelt, M.; Richter, B.; Naschitzki, M.; Bäumer, M.; Freund, H. J. Epitaxial Growth of SiO₂ on Mo(112). *Surf. Rev. Lett.* **2000**, *7*, 7–14.
- 31 Todorova, T. K.; Sierka, M.; Sauer, J.; Kaya, S.; Weissenrieder, J.; Lu, J. L.; Gao, H. J.; Shaikhutdinov, S.; Freund, H. J. Atomic Structure of a Thin Silica Film on a Mo(112) Substrate: A Combined Experimental and Theoretical Study. *Phys. Rev. B* **2006**, *73*, 165414.
- 32 Giordano, L.; Del Vitto, A.; Pacchioni, G. Au and Pd Atoms Adsorbed on Pure and Ti-Doped SiO₂/Mo(112) Films. *J. Chem. Phys.* **2006**, *124*, 034701.
- 33 Baron, M.; Stacchiola, D.; Ulrich, S.; Nilius, N.; Shaikhutdinov, S.; Freund, H. J.; Martinez, U.; Giordano, L.; Pacchioni, G. Adsorption of Au and Pd Atoms on Thin SiO₂ Films: The Role of Atomic Structure. *J. Phys. Chem. C* **2008**, *112*, 3405–3409.
- 34 Ulrich, S.; Nilius, N.; Freund, H.-J.; Martinez, U.; Giordano, L.; Pacchioni, G. Evidence for a Size-Selective Adsorption Mechanism on Oxide Surfaces: Pd and Au Atoms on SiO₂/Mo(112). *ChemPhysChem*, in press, DOI: 10.1002/cphe.200800153.
- 35 Sterrer, M.; Fischbach, E.; Risse, T.; Freund, H.-J. Geometric Characterization of a Singly Charged Oxygen Vacancy on a Single-Crystalline MgO(001) Film by Electron Paramagnetic Resonance Spectroscopy. *Phys. Rev. Lett.* **2005**, *94*, 186101.
- 36 Sterrer, M.; Yulikov, M.; Fischbach, E.; Heyde, M.; Rust, H. P.; Pacchioni, G.; Risse, T.; Freund, H.-J. Interaction of Gold Clusters with Color Centers on MgO(001) Films. *Angew. Chem., Int. Ed.* **2006**, *45*, 2630–2632.
- 37 Pacchioni, G.; Giordano, L.; Baistrocchi, M. Charging of Metal Atoms on Ultrathin MgO/Mo(100) Films. *Phys. Rev. Lett.* **2005**, *94*, 226104.
- 38 Sterrer, M.; Risse, T.; Heyde, M.; Rust, H.-P.; Freund, H.-J. Crossover from Three-Dimensional to Two-Dimensional Geometries of Au Nanostructures on Thin MgO(001) Films: A Confirmation of Theoretical Predictions. *Phys. Rev. Lett.* **2007**, *98*, 206103.
- 39 Sterrer, M.; Risse, T.; Martinez Pozzoni, U.; Giordano, L.; Heyde, M.; Rust, H.-P.; Pacchioni, G.; Freund, H.-J. Control of the Charge State of Metal Atoms on Thin MgO Films. *Phys. Rev. Lett.* **2007**, *98*, 096107.
- 40 Ho, J.; Ervin, K. M.; Lineberger, W. C. Photoelectron Spectroscopy of Metal Cluster Anions: Cu⁻ⁿ, Ag⁻ⁿ, and Au⁻ⁿ. *J. Chem. Phys.* **1990**, *93*, 6987–7002.
- 41 Ricci, D.; Bongiorno, A.; Pacchioni, G.; Landman, U. Bonding Trends and Dimensionality Crossover of Gold Nanoclusters on Metal-Supported MgO Thin Films. *Phys. Rev. Lett.* **2006**, *97*, 036106.
- 42 Lemire, C.; Meyer, R.; Shaikhutdinov, S. K.; Freund, H. J. CO Adsorption on Oxide Supported Gold: From Small Clusters to Monolayer Islands and Three-Dimensional Nanoparticles. *Surf. Sci.* **2004**, *552*, 27–34.
- 43 Lemire, C.; Meyer, R.; Shaikhutdinov, S.; Freund, H. J. Do Quantum Size Effects Control CO Adsorption on Gold Nanoparticles? *Angew. Chem., Int. Ed.* **2004**, *43*, 118–121.
- 44 Valden, M.; Lai, X.; Goodman, D. W. Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties. *Science* **1998**, *281*, 1647–1650.
- 45 Shaikhutdinov, S. K.; Meyer, R.; Naschitzki, M.; Bäumer, M.; Freund, H. J. Size and Support Effects for CO Adsorption on Gold Model Catalysts. *Catal. Lett.* **2003**, *86*, 211–219.
- 46 Bäumer, M.; Freund, H.-J. Metal Deposits on Well-Ordered Oxide Films. *Prog. Surf. Sci.* **1999**, *61*, 127–198.
- 47 Mullins, D. R.; Radulovic, P. V.; Overbury, S. H. Ordered Cerium Oxide Thin Films Grown on Ru(0001) and Ni(111). *Surf. Sci.* **1999**, *429*, 186–198.
- 48 Weiss, W.; Somorjai, G. A. Preparation and Structure of 1–8 Monolayer Thick Epitaxial Iron-Oxide Films Grown on Pt(111). *J. Vac. Sci. Technol. A* **1993**, *11*, 2138–2144.
- 49 Nilius, N.; Ernst, N.; Freund, H. J. Photon Emission from Individual Supported Gold Clusters: Thin Film versus Bulk Oxide. *Surf. Sci.* **2001**, *478*, L327–L332.
- 50 Benia, H. M.; Lin, X.; Gao, H. J.; Nilius, N.; Freund, H. J. Nucleation and Growth of Gold on MgO Thin Films: A Combined STM and Luminescence Study. *J. Phys. Chem. C* **2007**, *111*, 10528–10533.
- 51 Watanabe, K.; Menzel, D.; Nilius, N.; Freund, H. J. Photochemistry on Metal Nanoparticles. *Chem. Rev.* **2006**, *106*, 4301–4320.
- 52 Starr, D. E.; Shaikhutdinov, S. K.; Freund, H. J. Gold Supported on Oxide Surfaces: Environmental Effects as Studied by STM. *Top. Catal.* **2005**, *36*, 33–41.
- 53 Lu, J. L.; Gao, H. J.; Shaikhutdinov, S.; Freund, H. J. Gold Supported on Well-Ordered Ceria Films: Nucleation, Growth and Morphology in CO Oxidation Reaction. *Catal. Lett.* **2007**, *114*, 8–16.