

Pinning Mononuclear Au on the Surface of Titania

Lauren Benz, Xiao Tong, Paul Kemper, Horia Metiu, Michael T. Bowers, and Steven K. Buratto*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

Received: October 18, 2005; In Final Form: November 8, 2005

We have deposited Au atoms on the surface of titania without sintering or surface damage. Mass-selected Au^+ atoms were deposited from the gas phase at room temperature with kinetic energies from <3 to 190 ± 3.5 eV. Scanning tunneling microscopy reveals island formation following deposition at <3 eV, while mainly atomic features are observed for energies between ~ 35 and ~ 190 eV. A mixture of islands and atomic features is observed at a landing energy of 20 ± 3.5 eV, suggesting a critical energy above which pinning occurs. Cluster size is also probed as a function of coverage in the deposition of Au^+ with 100 eV of energy, revealing that sintering begins at a coverage of only 0.06 ML. These observations suggest a mechanism in which high-energy collision leads to the annealing of any impact-created surface damage and the pinning of Au atoms to the surface. We provide a new method of preparing isolated Au atoms on an oxide surface, which can serve as a platform for catalytic studies.

In bulk form, gold is regarded as chemically inert. However, surprising catalytic activity was discovered in the 1980s by Haruta and co-workers for supported gold nanoparticles on the order of 1 nm in diameter.¹ Since then, there has been an enormous amount of work to understand this remarkable behavior. Recently, mononuclear supported gold(III) and gold(I) centers formed from ionic complexes have been shown to catalyze CO oxidation and the water–gas shift reaction under ambient reaction conditions.^{2–4} In the case of CO oxidation, Guzman and colleagues demonstrated that the metallic gold clusters typically credited as the working catalysts are not solely responsible for the reactivity of these systems.⁴ It is speculated that these larger clusters may actually serve as CO reservoirs to active cationic mononuclear centers.² Size-selected studies have also been performed on supported small gold clusters in ultrahigh vacuum (UHV) conditions (model catalysts), revealing that deposited Au_1 exhibits nearly zero catalytic activity, while Au clusters seven or eight atoms in size are quite active.^{5,6} This apparent discrepancy may be the result of a difference in the oxidation state and/or reaction conditions. It may also be due to the strong sintering of Au atoms on the surface of titania at room temperature, which makes it difficult to prepare a surface decorated with single atoms. It is well-known from room-temperature vapor deposition studies that Au monomers are mobile on the surface of titania, forming islands several atomic layers in size.^{7,8}

In this letter, we probe the deposition of size-selected Au^+ on the surface of single-crystal rutile titania (110)–(1 \times 1) as a function of deposition energy using UHV scanning tunneling microscopy (STM). It has been known for sometime that it is possible to produce epitaxial thin films of metal on an oxide surface via energetic cluster impact.^{9,10} We now apply that idea to the single atom case on the surface of titania and find that,

at a critical threshold energy, sintering can be prevented, resulting in the formation of pinned Au atoms on the surface. We also explore the mechanism by which pinning occurs by monitoring cluster growth as a function of impact energy and as a function of Au coverage at an impact energy of 100 eV.

Au^+ ions are produced in a laser ablation source, which is described in detail elsewhere.^{11,12} The full width half-maximum (fwhm) energy spread of the ion beam was measured to be ~ 7 eV for an average ion having a kinetic energy of ~ 190 eV. Using ion optics, the beam is guided into a deposition chamber (deposition pressure $< 1 \times 10^{-9}$ Torr) where the titania sample is held normal to the incident cluster beam. During the low-energy deposition, the sample is positively biased at the average energy of the beam such that only ions in the high kinetic energy tail of the energy distribution reach the sample. Approximately 70% of the ions that reach the surface have a kinetic energy less than 3 eV. To achieve higher impact energies, the potential bias is lowered accordingly. Auger electron spectroscopy confirms that gold is present on the surface following deposition.

Prior to cluster deposition, the titania samples (Commercial Crystal Laboratories) were cleaned in UHV with cycles of argon ion bombardment (0.5–1 keV) and annealing to ~ 1000 K for 15 s intervals. A cluster beam intensity of ~ 1 nA/cm² was typical, therefore exposure times of ~ 30 min led to coverages of ~ 0.01 ML. The coverage observed agrees with the predicted coverage as measured from the cluster beam flux and exposure time to within a factor of ~ 2 , which is within experimental error. After cluster deposition, the sample was translated under vacuum into a separate chamber, in which the base pressure was $< 3 \times 10^{-10}$ Torr, and imaged using STM. STM images of the surface were acquired at room temperature on an RHK SPM 100 with typical operating parameters of a +1 to +2 V sample bias and a tunneling current of 0.1–0.2 nA. All reported diameters are fwhm values, and the heights are reported as

* Corresponding author. E-mail: buratto@chem.ucsb.edu.

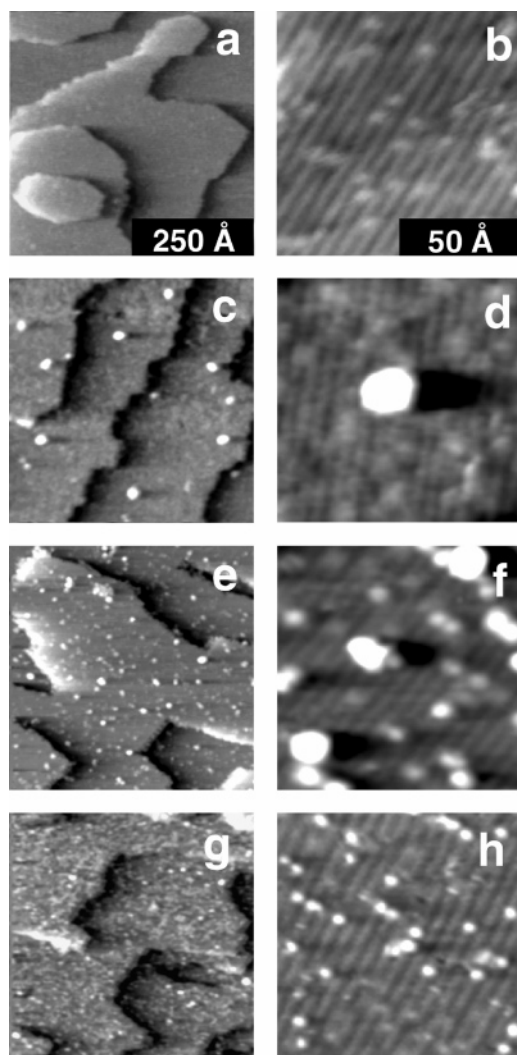


Figure 1. STM images (a,b) of a clean surface of titanium dioxide, with oxygen vacancies visible in (b) between 5-c Ti rows. (c–h) Surface of titania following the deposition of ~ 0.01 ML of Au^+ at various kinetic energies; (c,d) < 3 eV, (e,f) 20 ± 3.5 eV, (g,h) 190 ± 3.5 eV. Sintering occurs in the low-energy case, and a mix of atomic and multiautom features is seen following deposition at ~ 20 eV, while only atomic features are visible after deposition at ~ 190 eV. All images on the left are 500×500 Å and images on the right are 100×100 Å.

measured. No corrections have been made to account for tip convolution effects.

Figure 1a,b shows STM images of a clean TiO_2 (110)-(1 \times 1) substrate consisting of terraces a few hundred angstroms wide and steps ~ 3 Å high, the latter of which is in agreement with the expected step height for the rutile (110)-(1 \times 1) surface.¹³ The alternating bright and dark lines visible in 1b have been assigned to 5-fold coordinated titanium atom (5-c Ti) rows, and bridging oxygen atom rows, respectively,¹⁴ with a separation of ~ 6.5 Å between adjacent Ti atom rows. Between the titanium rows, bright features are visible, corresponding to vacant sites in the bridging O rows,¹⁴ which occupy $\sim 6\%$ of the bridging oxygen sites.

As seen in the STM images in Figure 1c,d, the deposition of Au^+ under soft-landing conditions (impact energy < 3 eV) results in significant sintering into cluster islands $\sim 4.3 \pm 1.7$ Å in height and $\sim 15 \pm 3.7$ Å in diameter, indicating that Au monomers are mobile at room temperature on the surface of titania. This result is similar to that observed in the deposition of Au from evaporative sources at similar coverages.⁷ Clusters are present at both step edges and on the terraces, where

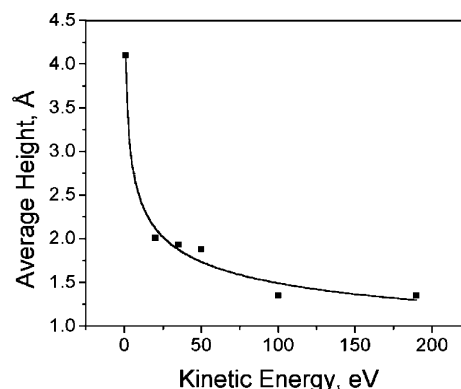


Figure 2. Plot of average feature height versus kinetic energy, which reveals that the critical pinning threshold occurs at ~ 20 eV.

nucleation may occur at intrinsic defect sites, including oxygen vacancies.^{15,16} The cluster distribution is broad, as described in more depth elsewhere,¹⁷ consisting of structures from 1 to 4 layers high. Vacancies are visible, but no other features are observed on the surface of titania between clusters.

When the deposition energy is increased to 20 ± 3.5 eV, a mixture of sizes is observed for the clusters as shown in Figure 1e,f. Sintered clusters are visible on the surface, similar in size to those observed under soft-landing conditions. In addition, a relatively high density of atomic-sized features, ~ 1.5 Å high and ~ 6.6 Å wide, also appears predominantly on the 5-c Ti rows.

Figure 1g,h shows the results of deposition at 190 ± 3.5 eV. The STM images show only atomic features ~ 1.4 Å high and ~ 4 Å wide, which are also located mainly ($> 80\%$ of observed features) over the 5-c Ti rows. The small feature size and good agreement with the predicted coverage lead us to assign these features as individual Au atoms. Close examination of the titania between these features reveals intact rows of titanium and oxygen atoms and oxygen vacancies, but no visible surface damage. The images acquired for depositions between 35 and 190 eV resulted in nearly identical features. It is interesting to note that these atomic features are very stable. They are present after annealing the sample to ~ 850 K for periods of 15 s, indicating a strong interaction between the Au atoms and the titania surface.

Following each experiment, the average cluster height was calculated and plotted in Figure 2. The graph shows a relatively sharp decrease in height when going from < 3 to ~ 20 eV of impact energy, suggesting that the critical pinning energy occurs in this region. The existence of both pinned and sintered features following the deposition of Au^+ with 20 ± 3.5 eV kinetic energy suggests that the onset of pinning occurs close to 20 eV.

The features we observe following high-energy impact (> 20 eV) are atomic in size and appear along the titanium rows, suggesting that Au atoms either selectively bind above the 5-c Ti atoms, or perhaps substitute for Ti atoms in the lattice. Vapor deposition studies of low coverages of Au on titania show evidence of cluster growth over 5-c Ti rows.¹⁸ The authors of this study presume that, after the oxygen vacancies are titrated by Au, growth continues preferentially over titanium atoms, although they are unable to resolve atomic features. Our results are not consistent with O-atom vacancies as the primary binding site since $> 80\%$ of the Au atoms are located along 5-c-Ti rows, and we deposit fewer Au atoms than there are vacancies. This is not unreasonable, however, since high-impact energies obviously alter the mechanism of cluster growth, possibly limiting access to vacancy sites.

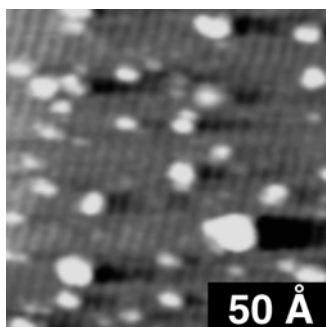


Figure 3. STM image of a titania surface after deposition of ~ 0.01 ML of Au^+ with ~ 190 eV kinetic energy, followed by ~ 0.01 ML Au^+ with <3 eV kinetic energy (deposition of only 0.01 ML of Au^+ at ~ 190 eV is shown in Figure 1g,h). Both sintered clusters and pinned atomic centers are visible, demonstrating that the surface is not damaged between pinned atoms during the deposition of Au at ~ 190 eV kinetic energy.

To confirm the apparent lack of surface damage in the high-energy experiments, we exposed the surface to ~ 0.01 ML of monomers at ~ 190 eV of energy, followed by ~ 0.01 ML of monomers with <3 eV kinetic energy. The result is shown in Figure 3. After the initial exposure, the sample has only atomic features on the surface, similar to those observed in Figure 1g,h. Following the second, low-energy deposition, a mixture of sintered, larger clusters, and pinned monomers are visible on the surface. If surface defect density had increased as a result of the high-energy deposition, one would expect the cluster density to increase significantly because of an increase in the nucleation events at defect traps, which we have previously shown in a similar system to effectively nucleate clusters.¹⁵ The cluster density did not change after the second deposition, suggesting that the low-energy deposition results in mobile monomers, which likely nucleate mainly at the preexisting pinned monomers. From this we conclude that there is no surface damage between pinned sites following high-energy depositions.

It is possible that the impinging monomers lack the momentum necessary to create widespread, permanent surface damage. In previous studies by Pratontep and colleagues involving high-energy collisions of Au_7 , Ag_7 , and Si_7 with graphite, crater formation was observed, and penetration depth was measured with STM as a function of kinetic energy.¹⁹ They found that implantation depth scales linearly with cluster momentum for both gold and silver at elevated impact energies, with the least implantation (~ 5 Å) occurring for clusters with roughly 120u Å/fsec of momentum. For our Au monomers, which have much lower momenta (27u Å/fsec at 190 eV kinetic energy), no cratering or other damage is observed on the titania surface.

In an attempt to better understand the pinning mechanism, we studied the effect of exposing the titania sample to higher coverages of Au with ~ 100 eV kinetic energy. Figure 4 shows STM images of successive depositions of Au onto a titania surface up to a coverage of ~ 0.085 ML. After the first and second depositions (a and b, respectively), resulting in total coverages of ~ 0.012 and ~ 0.036 ML, respectively, only Au atoms are observed on the surface. An average height of 1.3 ± 0.3 Å is found for these features. Further deposition (total 0.06 ML; Figure 4c) results in the formation of small clusters <10 atoms in size, measuring 2.1 ± 0.7 Å high, and in a decrease in feature density. The broad distribution in feature height is indicative of sintering. A final exposure (total ~ 0.085 ML; Figure 4d) results in a surface that appears largely unchanged with the exception of a slight increase in the average feature height to 2.3 ± 1 Å. Figure 5 plots these results, showing a

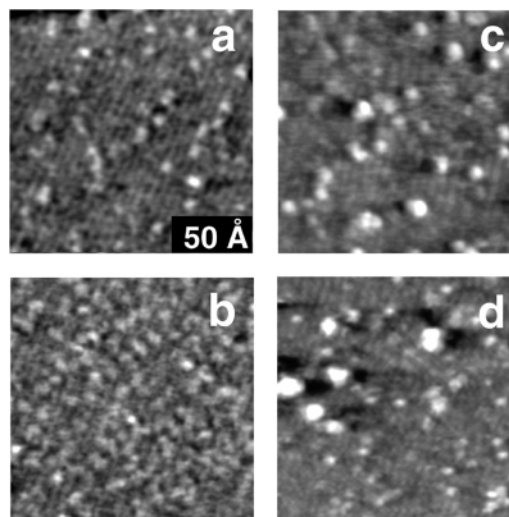


Figure 4. STM images of the titania surface following successive depositions of Au^+ with ~ 100 eV kinetic energy. Total coverages are: (a) 0.012 ML, (b) 0.036 ML, (c) 0.06 ML, and (d) 0.084 ML. At 0.06 ML, larger clusters are visible, indicating that localized heating occurs from the impact of incoming ions, leading to sintering.

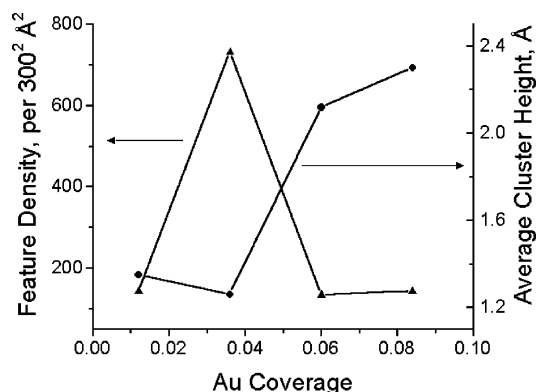


Figure 5. Feature density and average cluster height are plotted as a function of coverage for deposition of Au^+ with ~ 100 eV kinetic energy.

clear increase in feature height with coverage at the expense of feature density after 0.06 ML of Au has been deposited. These results imply that sintering occurs as the result of high-energy deposition at coverages as low as 0.06 ML. Since the coverages tested here are much less than a monolayer, sintering is unlikely to occur from incoming atoms impinging on preexisting pinned atoms. We attribute this sintering to localized heating around the ion impact zone. Just prior to sintering (Figure 4b), the feature centers are separated by approximately 15 Å. This distance can therefore be assigned as the upper limit of the effective heating radius. Since annealing the surface to ~ 850 K did not result in the sintering of pinned atoms, the local heating that results from impact must be greater than 850 K.

The above-presented data suggests the following pinning mechanism: Upon impact, a localized, high-temperature region is created as the atom hits the surface, as evidenced by the observed sintering at low coverages at a deposition energy of 100 eV. As this energy dissipates, any transiently formed surface deformations/defects must be annealed, since no surface damage is present between clusters following high-energy deposition. We acknowledge, however, that STM alone cannot specifically reveal the nature of the surface directly below the observed Au atoms; therefore, we do not completely rule out the possibility of a defect directly below the Au atom, (i.e., a Au atom may substitute for a Ti atom, binding at a 5c-Ti site); however, given

the fact that the surface between features appears pristine, we find this unlikely. In studies of high-energy cluster–substrate collisions of other systems, molecular dynamics simulations predict a similar outcome, with impact temperatures on the order of thousands of degrees Kelvin and epitaxial growth following impact at energies of 5–10 eV per atom.^{20,21} Despite the fact that these studies involved large metallic clusters and metallic substrates, this impact threshold agrees qualitatively with our pinning energy of ~20 eV. The selective appearance of gold atoms at 5c-Ti sites is evidence that the Au atoms have much lower mobility following high-energy impact than they do in the case of soft-landing, preventing sintering from occurring. This lack of mobility is likely the result of the association of the impinging Au atoms with impact-created defects immediately following impact, before the defects have been annealed. The Au atoms remain near the temporarily defective surface, and bind either at or above a nearby 5c-Ti site during the recovery process.

In summary, we find that it is possible to prepare Au atom-decorated titania surfaces by the high-impact deposition of Au⁺. The minimum kinetic energy necessary to pin Au atoms to the surface of titania is ~20 eV. Because of a lack of observable surface damage and sintering at low coverages following high-energy deposition, we propose the high-energy Au⁺ impact results in a localized heating of the surface and an annealing of any created defects. Following impact, a gold atom is pinned either at or above a 5c-Ti site. A coverage-dependence study of Au⁺ with ~100 eV kinetic energy demonstrates an approximate heating radius of 15 Å and a lower limit local temperature of 850 K in the impact zone. Exploring these monatomic Au centers for possible catalytic activity is currently underway.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research under the Defense University Research Initiative on Nanotechnology (DURINT), contract number F49620-01-04J9. We would also like to thank the following people: Dr. Steeve Chretien for his useful input; Dr.

Andrei Kolmakov for his help in the design and construction of the apparatus as well as for many insightful conversations; Dr. Yigal Lilach for useful discussions and experimental assistance; and Manuel J. Manard for assistance with the construction of the apparatus.

References and Notes

- (1) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301.
- (2) Fierro-Gonzalez, J. C.; Gates, B. C. *J. Phys. Chem. B* **2004**, *108*, 16999.
- (3) Fu, Q.; Deng, W. L.; Saltsburg, H.; Flytzani-Stephanopoulos M. *Appl. Catal., B* **2005**, *56*, 57.
- (4) Guzman, J.; Kuba, S.; Fierro-Gonzalez, J. C.; Gates, B. C. *Catal. Lett.* **2004**, *95*, 77.
- (5) Sanchez, A.; Abbet, S.; Heiz, U.; Schneider, W. D.; Hakkinen, H.; Barnett, R. N.; Landman, U. *J. Phys. Chem. A* **1999**, *103*, 9573.
- (6) Lee, S.; Fan, C.; Tainpin, W.; Anderson, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 5682.
- (7) Spiridis, N.; Haber, J.; Korecki, J. *Vacuum* **2001**, *63*, 99.
- (8) Zhang, L.; Persaud, R.; Madey, T. E. *Phys. Rev. B* **1997**, *56*, 10549.
- (9) Haberland, H.; Karrais, M.; Mall, M.; Thurner, Y. *J. Vac. Sci. Technol., A* **1992**, *10*, 3266.
- (10) Yamada, I. *Appl. Surf. Sci.* **1989**, *43*, 23.
- (11) Kemper, P. K.; Bowers, M. T., to be submitted for publication.
- (12) Benz, L.; Tong, X.; Kemper, P.; Lilach, Y.; Kolmakov, A.; Metiu, H.; Bowers, M. T.; Buratto, S. K. *J. Chem. Phys.* **2005**, *122*, 081102.
- (13) Onishi, H.; Iwasawa, Y. *Surf. Sci.* **1994**, *313*, L783.
- (14) Diebold, U.; Anderson, J. F.; Ng, K. O.; Vanderbilt, D. *Phys. Rev. Lett.* **1996**, *77*, 1322.
- (15) Tong, X.; Benz, L.; Kolmakov, A.; Chretien, S.; Metiu, H.; Buratto, S. K. *Surf. Sci.* **2005**, *575*, 60.
- (16) Wahlstrom, E.; Lopez, N.; Schaub, R.; Thostup, P.; Ronnau, A.; Africh, C.; Laegsgaard, E.; Norskov, J. K.; Besenbacher, F. *Phys. Rev. Lett.* **2003**, *90*, 026101.
- (17) Tong, X.; Benz, L. B.; Kemper, P.; Metiu, H.; Bowers, M. T.; Buratto, S. K. *J. Am. Chem. Soc.* **2005**, *127*, 13516.
- (18) Lai, X.; St. Clair, T. P.; Valden, M.; Goodman, D. W. *Prog. Surf. Sci.* **1998**, *59*, 25.
- (19) Pratontep, S.; Preece, P.; Xirouchaki, C.; Palmer, R. E.; Sanz-Navarro, C. F.; Kenny, S. D.; Smith, R. *Phys. Rev. Lett.* **2003**, *90*, 055503.
- (20) Haberland, H.; Insepov, Z.; Karrais, M.; Mall, M.; Moseler, M.; Thurner, Y. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1993**, *80–1*, 1320.
- (21) Betz, G.; Husinsky, W. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1997**, *122*, 311.