Formation and Stabilization of Nano-Sized Pt Clusters on TiO_2 Surfaces

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Abstract

This paper reports experiments related to the stability and size distributions of platinum (Pt) clusters on TiO_2 surfaces. Efforts to enhance the efficiency and reliability of microsystems will likely use components or elements with at least one dimension smaller than a micron. The ability to design and fabricate elements at submicron dimensions—nanotechnology—is a rapidly growing area of science and technology. In this paper we describe experiments using newly generated knowledge of surfaces and the nanodimensional information provided by scanning probe microscopy (SPM) that are designed to assist development of a new generation of catalysts for application in microchemical systems. Critical questions for the design of new catalysts is the ability to fabricate metal clusters of different sizes and their temperature stability. We report on the investigation of nucleation, growth, and temperature stability of self-organized nanoscale Pt clusters on different TiO_2 surfaces using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). Surfaces examined include anatase (001) and rutile (110), both (1x1) and reconstructed (1x2) forms.

Introduction

Microchemical systems are generally optimized for transport of critical chemical components to and from the reaction site. When transport limitations are removed, surface reaction rates (e.g., for catalytic systems) may become the rate-limiting process. Thus, microchemical systems may benefit if we can design and produce catalysts with optimized geometry and efficiency. We are using new techniques and information about surfaces to stabilize the distribution and size range of metal clusters on rutile and anatase (TiO_2) surfaces.

Oxide-supported metal clusters are common forms of catalysts. Our objective has been to attempt to engineer or design surfaces where the distribution of the clusters was better known and controllable than in standard powder catalytic materials. This goal is not unique; others are working at it in different ways. The Somorjai group at Berkeley, for example, is using microfabrication methods to create arrays of catalyst materials using lithography (Yang et al. 1998). No matter what approach is used, important questions about nanodimensional structures include the need to determine (or verify) the nature of the structure formed and to measure the temperature stability. There can be significant uncertainty about the ability of some nanodimensional structures to survive in different environments. Some of the many processes that could destroy or alter a nanodimensional system are contamination or fouling, corrosion, interfacial compound formation and surface diffusion. One of our first objectives in the effort to create well-defined nanodimensional distributions on an oxide surface was to somehow stabilize these clusters to minimize their growth.

Surface Stabilization of Nanoclusters

It is well established that many of the interactions of a surface with materials take place at steps on the surface. One of our initial thoughts was to create a well-defined stepped surface and stabilize the metal clusters by having them attach to steps. This concept is shown in Figure 1. In this concept, Pt (or another metal) is evaporated onto a well-

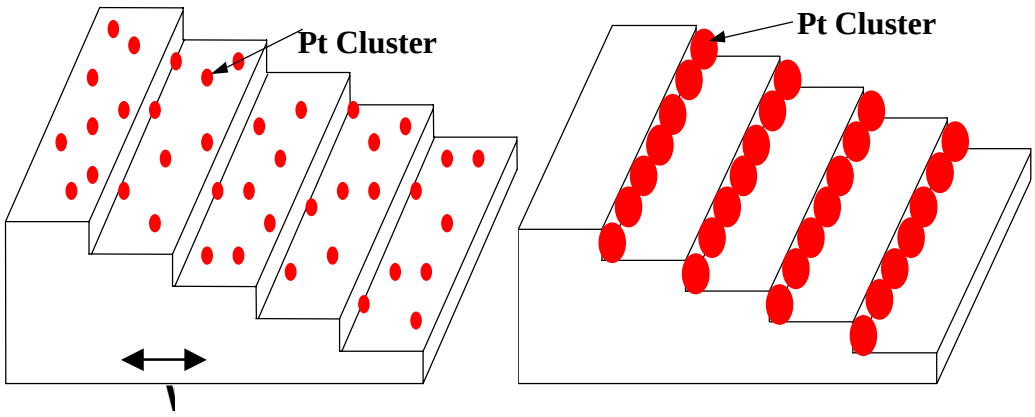


Figure 1. Schematic Drawings Showing the Random Formation of Metal Clusters on the Terraces of Stepped Surfaces and the Migration of these Clusters to the Steps where they are Attached and Resistant to Further Growth

defined oxide surface with a series of steps. The size of the clusters and the final density will be determined by separation of the steps, the temperature of the surface during the metal evaporation, and the rate of metal evaporation. In this approach, we are attempting to use various aspects of the surface structure to control the size, position, and stability of the clusters.

The first barrier to achieving this for an oxide substrate is preparation of the surface. The preparation of metals and semiconductors with well-defined step structures is well established. Usually these materials are polished at some angle just off a high-symmetry direction and, after cleaning and heating in vacuum, a nice step structure is formed. Unfortunately, the preparation of the surfaces of compound materials is much more complex (Diebold 1998). Consequently, the first part of this project required learning to prepare the appropriate surfaces.

The foundation of the work reported here builds upon the wonderful observations capabilities of new scanning probe systems and significant new levels of information about oxide surfaces, particularly TiO_2, they have made possible. Because the surfaces of transition metals oxides play important roles in a wide variety of technologies, including sensors, fuel cells, catalysts, and, to an increasing extent, electronic devices, a strong interest has developed in obtaining a more detailed understanding of their surface structure and chemistry. To a significant degree, TiO_2 serves as both a model oxide system and a material of technological importance. Consequently, a significant effort has been devoted to understanding many properties of various TiO_2 oxides. Of particular importance, recent scanning probe work using primarily scanning tunneling microscopy (STM) has provided a significant advancement in the understanding of the details of the surface structures of these oxides (Diebold et al. 1996; Xu et al. 1997; Onishi and Iwasawa 1996; Pang et al. 1998; Bennett 1999). Our work used this new knowledge and ability to alter and observe surface structures to examine the interactions of metal clusters on different surfaces. This work is also facilitated by the considerable work performed on the interactions of metals on rutile surfaces that has been summarized by Diebold and Madey (Diebold et al. 1995).

The approach used in this study is to prepare well-defined surfaces of TiO_2 oxides onto which Pt can be deposited. The STM is used both to determine the initial surface and to observe the nature of the clusters that form during the metal deposition and upon further annealing.

Experimental

The experiments were conducted in a custom-designed ultra-high vacuum (UHV) system that consists of a surface processing and analysis chamber, an STM chamber, and a loadlock. The first chamber is equipped with oxygen plasma (Wavemat Inc.), a sputtering gun, an XPS (VG Scientific), a metal evaporation source, and a low energy electron diffraction (LEED) (Princeton). The second chamber houses an STM (Park Scientific Instruments) and is separated from the main chamber by two gate valves. The base pressure in these two chambers is $2x10^{-10}$ Torr.

Samples were mounted on transferable sample platens with an attached chromel-alumel thermocouple for direct temperature measurement. The sample can be transferred between the chambers under UHV conditions. The oxygen plasma ($2x10^{-5}$ Torr of oxygen partial pressure, 200 W power) was operated 7.6 cm away from the sample surface. The species from the plasma source consists of molecular oxygen, atomic oxygen, and oxygen ions with energies ranging from 10 to 30 eV.

Rutile TiO_2 (110) single crystals (±0.5°, Princeton Scientific Corp.) or anatase (001) single-crystal thin films grown by oxygen-plasma assisted molecular-beam epitaxy (OPA-MBE) were ultrasonically cleaned in acetone and methanol before being loaded into the UHV system. The specimen cleaning and processing procedure required some development (Gan et al. 1999). Our most recent cleaning method involves annealing specimens in vacuum and then exposing them to an O_2 plasma. However, some specimens were prepared by a combination of ion sputter bombardment and annealing in vacuum. After these treatments, the TiO_2 substrates were analyzed by XPS, LEED, and STM to determine the surface composition and structure. The same analysis was performed on the surfaces after small amounts of Pt deposition. .

Most experiments involve preparing the surface to the desired condition, evaporating Pt onto the surface, observing the Pt distribution, heating the specimen and observing changes in the Pt distribution. The ability to form different structures on the rutile (110) surface is demonstrated in Figure 2a, which is an STM image of the rutile (110) (1x1) surface structure obtained after processing it first in oxygen plasma and then in UHV conditions. Atomic rows and well-defined steps are clearly evident. Extended annealing in UHV condition along with a few circles of argon ion sputtering produces the reconstructed rutile (110) (1x2) surfaces shown in Figure 2b, where (1x2) atomic rows and cross-linking structures (rows running from lower left corner to upper right corner) are both evident.

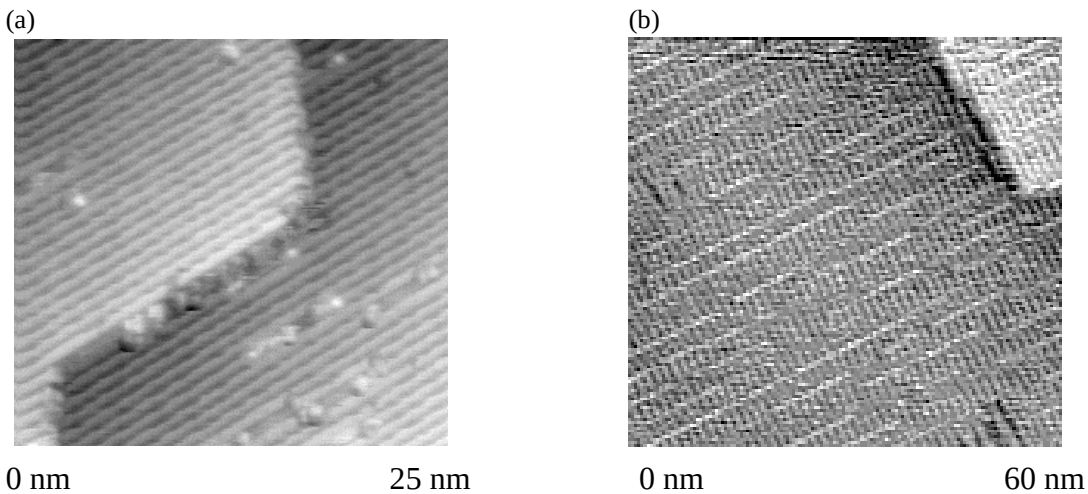


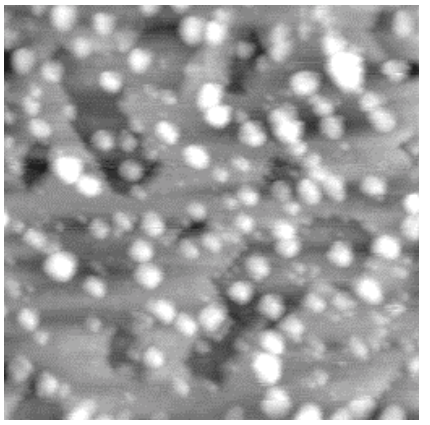
Figure 2. STM micrographs of the rutile TiO2 (110) surface showing a) 25x 25 nm^2 image of the (1x1) structure of a rutile (110) surface, and b) 60 x 60 nm^2 image of the reconstructed (1x2) phase on a rutile (110) surface

Results

By processing specimens in different ways it is possible to get a variety of surface structures. In the following we describe the interactions of Pt clusters with the rutile (110) unreconstructed 1x1 surface, Pt clusters on the rutile reconstructed 1x2 surface, a stepped rutile (110) surface with both 1x1 and 1x2 structures, and an anatase (001) 1x1 surface.

Rutile (110) 1x1 and 1x2 surfaces—Figure 3 is an STM image of Pt deposited on a rutile (110) 1x1 surface. These clusters were deposited by evaporating 0.5 ML (monolayers) of Pt onto the surface at ambient temperature. Subsequent annealing of the sample at 600 and 650K caused significant growth in the cluster size.

Figure 3. STM image of Pt clusters formed on a rutile (110) 1x1 surface

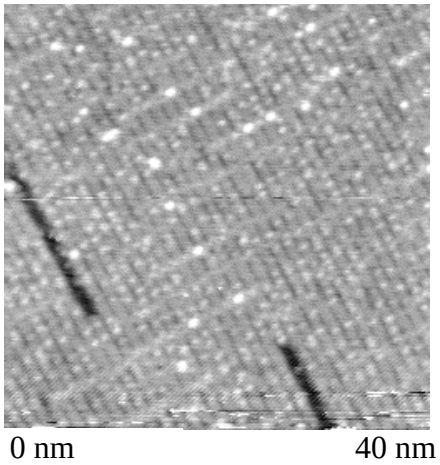


Cluster information:

Condition	mean size	FWHM300K(as deposited, 1.4 nm 1 nm)
600K	1.6 nm	0.7 nm
650K	2.0 nm	0.8 nm

A similar set of experiments carried out for a rutile (110) surface annealed in vacuum long enough to produce 1x2 reconstruction. The spacing between rows is eventually twice as far apart as the 1x1 surface, but the rows appear widely spaced initially. Eventually, enough form to have a surface with a 1x2 order. The (1x2) structure appears to have a stronger interaction with Pt clusters because the size distribution of Pt clusters does not change when heated to 600K. Pt clusters primarily attached to top of the (1x2) rows, as shown in Figure 4.

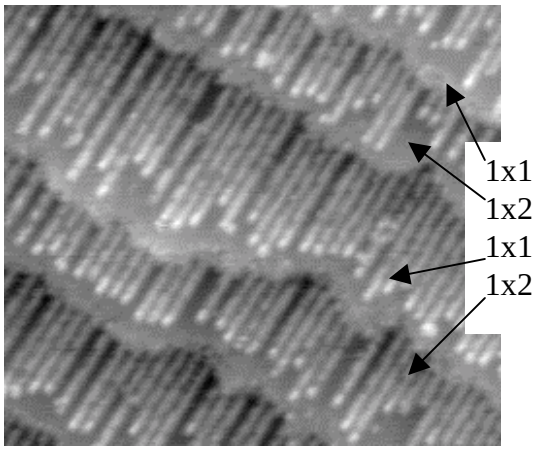
Figure 4. A 40x40 nm^2 STM image showing Pt nanoclusters primarily attached to the top of 1x2 atomic rows. These Pt clusters appear to have higher thermal stability.



Condition	Size	FWHM
300K (as deposited)	0.84 nm	0.12 nm
600K	0.84 nm	0.12 nm

One interesting observation is that, on stepped surfaces of rutile (110), both 1x1 and 1x2 structures can be produced in an organized fashion. In particular, when a series of steps is present, it is possible to have steps that alternate between the 1x1 and1x2 structures, as shown in Figure 5a. Based on these results, it might be assumed that Pt clusters would prefer the 1x2 surface. Deposition of Pt on the dual structure stepped surface confirms this guess (Figure 5b).

(a)



(b)

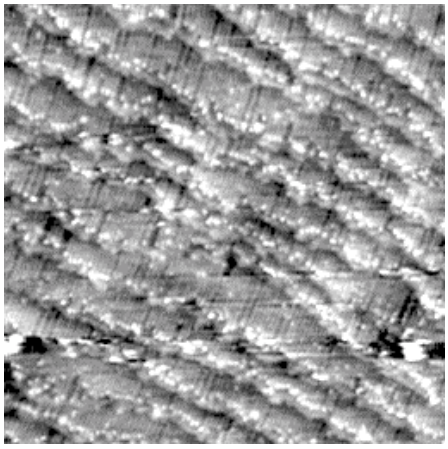
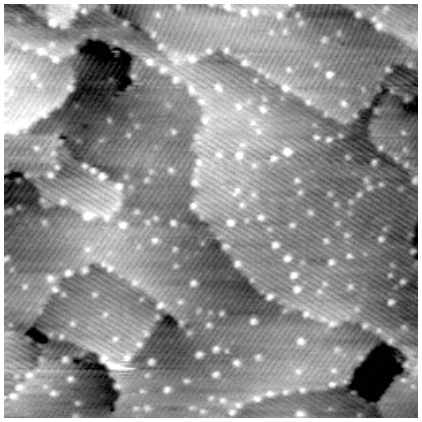


Figure 5. STM Image of (a) Stepped Rutile (110) Surface with Both 1x1 and 1x2 Structures;. b) Stepped Surface with Both 1x1 and 1x2 Structures Showing that Pt Clusters Selectively Adhere to Edges of the 1x2 Structure. In this case, the mean particle size is 1.4 nm; the FWHM of the distribution of 0.5 nm.

Anatase (001) Surface—Because of the difficulty of getting single=crystal specimens, the anatase surface is less well examined than most rutile surfaces. In this study, a (001) surface of anatase was grown by oxygen-plasma assisted MBE. The data that follow provides for this unique surface the type of data reported above for the rutile (110) surface. Careful observation of Figure 6 will show some degree of preference for clusters to occupy step sites. Although these clusters grow somewhat in size upon heating, they appear to reach a somewhat stable configuration. They appear to reach a stable size, and the distribution narrows.



0 nm 120 nm

Figure 6. STM images of Pt clusters on the anatase (001) surface.

Condition	mean size	FWHM
420K	1.5 nm	0.5 nm
520K	1.73 nm	0.23 nm
670K	1.77 nm	0.22 nm

Conclusions

These measurements demonstrate that it is possible to control the size distribution and stability of metal clusters on oxide surfaces by varying the atomic structure of the surfaces. The clusters can be formed by a self-organization process and stable to temperatures above 650K on the proper substrate. Based on these results it should be possible to form a wide variety of cluster sizes. The next important question involves determining the chemical properties of the clusters as the substrate, density, distribution, and size are altered. Measurements of the chemical differences in these materials are under way.

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