Dynamic restructuring of gold surfaces during chemical reactions

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Résumé   **Restructuration dynamique de surfaces d'or au cours de réactions chimiques**

Jacques-Émile Dubois a été l'un des premiers à développer la visualisation tridimensionnelle des molécules en utilisant les moyens informatiques et les données expérimentales. Il est maintenant possible d'imager et de visualiser les atomes et les molécules sur une surface avec les techniques modernes de la physico-chimie. Contrairement aux prévisions, des solides en apparence inertes présentent au niveau de leurs surfaces une grande activité. Ainsi, même à température ambiante, les atomes et molécules se déplacent constamment sur la surface. Cet article montre dans le cas de surfaces d'or comment certaines espèces chimiques gazeuses susceptibles de se lier aux atomes de surface facilitent ce mouvement d'atomes. Cette « danse » des atomes de surface constitue une propriété essentielle que l'on retrouve dans tout processus de catalyse ainsi que dans l'utilisation des dispositifs de microélectronique.

Mots-clés   **Surfaces d'or, microscopie à effet tunnel (STM), diffusion d'atomes de surface, restructuration de surface, déposition de soufre, réactions de surface.**

Abstract   Professor Jacques-Émile Dubois pioneered the field of molecular visualization using molecular models constructed from experimental data. It is now possible to image and visualize atoms and molecules on solid surfaces using modern tools of surface chemistry and physics. Contrary to our expectations, seemingly immutable solids are teeming with activity on their surfaces. Atoms and molecules move around on the surface, even at room temperature. This article shows how species that bind to the surface from surrounding gases facilitate movement of surface atoms using gold surfaces to illustrate this phenomenon. The "dance" of atoms on surfaces is an essential property for important processes, such as catalytic chemical synthesis and use in microelectronic devices.

Keywords   **Gold surfaces, scanning tunneling microscopy (STM), diffusion of surface atoms, reconstruction, sulfur deposition, release surface reactions.**

V isualization is a key tool in science. Chemists, in particular, rely on visual models of molecular structure as a means of developing intuitive methods for predicting chemical behavior. Indeed, Professor Jacques-Émile Dubois was well-known for his ground-breaking work in visualizing and classifying molecular structure. Historically, molecular modes have been derived from spectroscopic and diffraction methods that are sensitive to structure, oftentimes augmented by theoretical studies. While these methods have been powerfully applied to molecular systems, the study of chemical reactions and structure on solid surfaces poses a challenge to these traditional approaches: since the atoms on the surface are only a small fraction of the material, tools used for molecular systems are not readily applied.

The study of solid surfaces is important because they are ubiquitous in our world – the minerals and materials that form our earth provide the means for making great structures, tools and useful devices. These same materials can also act as agents of chemical change. Heterogeneous catalysts, on which the world relies to produce materials for our use and to keep our environment clean, are solid surfaces that promote and participate in chemical reactions. One example of an important application of surface chemistry is the "catalytic converter" present in automotive exhaust systems. The catalytic converter has dramatically improved the air quality in urban environments over the past few decades, saving lives, improving quality of life and reducing destruction due to acid rain [1-2]. Another example is the synthesis of organic oxygenates that are important for the manufacture of synthetic materials and alternative fuels. Corrosion of materials used in,

e.g. construction, motorized vehicles, or even artwork, is another important area of surface chemistry that has major world-wide economic impact. Frictional behavior is yet another area that depends on surface chemistry. Clearly, the study of chemical events on surfaces is widely important.

The 2007 Nobel Laureate in Chemistry, Prof. Gerhard Ertl, is greeted by Professor Cynthia Friend at a reception celebrating the award at Prof. Ertl's home institution, the Fritz Haber – Institut der Max-Planck-Gesellschaft, in Berlin Germany (www.fhi-berlin.mpg.de). Profs. Friend and Madix are on Alexander von Humboldt Awardees and are visiting the laboratory of Prof. H.-J. Freund at the Institut during their sabbaticals. Photo was taken by Prof. Robert Madix.

Unlocking the secrets of chemical reactions on surfaces has been a long-standing goal. Because of recent advances in our ability to image surfaces, it has become clear that the dynamic nature of solid surfaces is essential to their chemical activity. Even though solid surfaces seem to be immutable to

Professor Cynthia Friend and several members of her research group in the laboratory with a scanning tunneling microscope system used for imaging surfaces at the atomic scale, covered with aluminum foil. From left to right: Ms. Xiaoying Liu, Chemistry graduate student, Prof. Friend, Mr. Ryan Quiller and Dr. Dilini Pinnaduwage, recent doctoral recipient in Applied Physics, and Mr. Thomas Baker, Chemistry graduate student. (The photo was taken by Dr. Weiwei Gao, a postdoctoral fellow in the group and an accomplished photographer).

the eye – just that, "solid" – these same surfaces are teeming with activity on the length scale of atoms. Atoms and molecules are moving around, rearranging themselves, even at moderate (near room) temperature. Indeed, this "dance" of surface atoms is affected by molecules that are on and around the surface. In this article, I use our studies of gold surfaces to illustrate the lability of solid surfaces and the multifunctional characteristics of gold.

Visualizing atoms on surfaces

We are not able to see the atoms moving on the surface with our eyes or even with typical optical microscopes because they are so tiny. The size of a typical atom is approximately 20 000 times smaller in diameter than a typical hair. We can see hair because it has a size that is about 10 times larger than the wavelength of visible light. Since atoms and molecules are so much smaller than visible light, our eyes cannot see individual atoms and molecules even with optical microscopes. As a result, a different means of "seeing" atoms needed to be developed for us to probe matter at this length scale. Indeed, the need for developing tools of various sorts to help us visualize atoms and molecules has driven many experimental and theoretical advances in chemistry, physics and biology.

Our ability to see atoms and molecules moving on solid surfaces is possible because of a tool named scanning tunneling microscopy (STM). The STM was first developed by two scientists, Binnig and Röhrer, who won the Nobel Prize in physics in 1986 for their work [3-4]. The scanning tunneling microscope itself is elegantly simple, but relies on having an extremely quiet environment because very precise positioning of a sharp metal tip relative to the surface being studied is required. This important tool is based on the quantum mechanical behavior of electrons in both the tip and the

surfaces being studied. A quantum mechanical description of the behavior of electrons predicts that electrons can pass through vacuum between two materials even if their kinetic energy is too low to cross over the barrier for electron transfer. This phenomenon is called "tunneling" because it is analogous to a particle passing *through* a mountain instead of traversing the summit. The probability of this tunneling behavior is very small and decreases rapidly (exponentially) as the separation of the two materials increases. Tunneling also only occurs to a measurable degree for very tiny particles, such as electrons, not for macroscopic objects, like a baseball. Binnig and Röhrer recognized that a topographic image of surfaces could be obtained by scanning a conducting tip parallel to a surface and mapping the current that flows due to tunneling between the surface and the tip. In this way, atoms can be visualized on the surface. Binnig and Röhrer successfully implemented the technique in 1981. A particularly elegant example, from the work of Eigler *et al.*, who arranged and visualized atoms at extremely low temperature (near absolute zero) where atoms are frozen on the surface, illustrates the technique (*figure 1*).
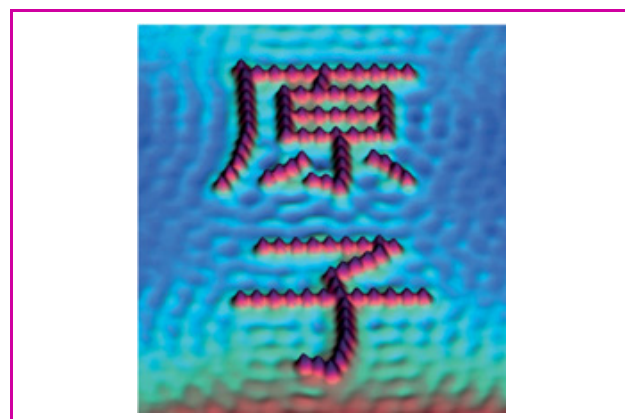

Figure 1 - Scanning tunneling microscope image of Fe atoms (in red) arranged on a Cu surface at low temperature (4 K) in the form of the Japanese kanji symbol for atom from the work of Don Eigler, IBM Rearch. The low temperature prevents diffusion of the Fe atoms on the surface during imaging (used with permission).

Binnig's and Röhrer's achievement – the implementation of the tunneling phenomenon to image surfaces – has revolutionized our study of surfaces and interfaces. Over the past two decades, there have been numerous technical improvements and the development of commercial instrumentation for STM, which have made it a widely accessible tool. This tool has made visualization of atoms and molecules on surfaces possible.

With the STM, we are able to image surfaces before, during and after a reactions occurs. Thus, we are able to take snapshots of the surface and to generate movies showing how the surface evolves. These experiments show that surfaces are dynamic in nature and that the reactive processes affect the structures that are present and the movement of atoms on the surface.

Why surfaces are different

The dynamic nature of surfaces is a consequence of the fact that surface atoms experience a different environment from atoms in the interior (bulk) of a solid. By creating a surface, the atoms on the surface lose many of their neighbors. The loss of neighboring atoms creates an environment that is
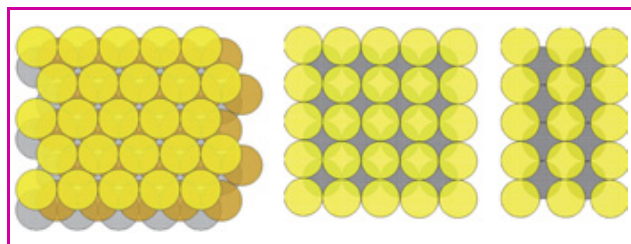
Figure 2 - Schematic representation of three different planes of a face centered cubic crystal such as gold based on the arrangement of atoms in the bulk of the solid.
The arrangement of atoms in the plane depends on the surface plane exposed. Gold surfaces change their geometric structure when they are created in order to compensate for loss of neighboring atoms that were removed upon creation of the surface. The yellow circles denote the top layer, grey the second layer and the dark gold circles the third layer. The surfaces shown are referred to as (111), (100) and (110). (figure provided by Mr. Thomas Baker).

not as energetically stable as the bulk. The loss of the neighbors affects the distribution of electrons around the surface atoms and, consequently, atoms at the surface rearrange to a different geometric arrangement than would be present in the bulk. Generally, surface atoms rearrange so as to make up for their loss of coordination to neighbors because it is energetically favorable to increase their local density on the surface. At the same time, the rate at which a surface can rearrange *and* the specific structure formed will depend on the surface temperature.

The rate of rearrangement of surfaces is dictated by the diffusion rate of atoms on the surface, which is related to the strength of bonding. Diffusion or migration of atoms across the surface also depends on the surface temperature, because this determines the kinetic energy of the atoms. To diffuse on a surface, an atom must partially break bonds with the surface, essentially skating around on a bumpy surface. The corrugation in the surface is the result of different types of coordination sites on the surface (*figure 2*). Generally, atoms favor high coordination sites and diffusion across the surface requires loss of coordination, if only temporarily. Moving across the surface creates a bumpy potential energy landscape for the atoms. The height of the barriers to diffusion is related to the strength of the bonding of the atom to the surface. Usually, the energy barrier to diffusion is 0.1-0.3 times the binding energy of the atom to the surface. For a pure material, the energy cost of diffusion is proportional to the heat of sublimation. A qualitative sense of the strength of bonding can be obtained by considering the relative melting points of various materials. In the case of the iron atoms on the copper surface in *figure 1*, diffusion was minimized by performing experiments at extremely low temperature (4 degrees Kelvin, near absolute zero).

The most favorable structure on the surface also depends on temperature because both energy and entropy (a measure of disorder) play a role. Entropy plays an increasing role as temperature is increased. The surface is most stable when the surface tension (also called the surface free energy which is a measure of the balance between energy and entropy) is at a minimum. Manifestations of surface tension can be observed in every day life by observing liquid drops. For example, a drop of water will bead up on some surfaces and spread out or "wet" others. These behaviors are a property that we can see on a larger scale, but that are due to interactions that occur on a small (molecular) scale. On solid surfaces, the effect of surface tension is also manifested on a smaller scale.

We will use a surface of gold to illustrate how the structure of a surface is generally different from the same plane in the bulk of the material. The specific surface we have studied is referred to as the (111) plane, which identifies the plane through which the crystal is cut. The structure of the plane depends on how you cut the crystal, as illustrated in *figure 2*. The structures of these two different planes are those corresponding to that plane in the interior of the gold. However, these structures are not the most stable for the clean gold surfaces because when the surfaces are exposed to vacuum, the atoms and the electrons associated with the atoms rearrange to a more stable and densely packed structure to offset the loss of their neighbors that had been in the plane above before the surface was created.

The Au(111) surface rearranges to a complex structure referred to as the "herringbone" structure, so named because the arrangement of atoms leads to a pattern that resembles a herringbone suit – but it is on an atomic scale! The Au(111) surface plane actually has more atoms per unit area than the same plane in the bulk – 4.2% more. These extra atoms come from defects, in particular one atom high "steps", that are present to some extent on all surfaces at finite temperature (these defects are the consequence of entropy and will be discussed more below).

A model of the herringbone structure shows that the Au atoms on the surface increase their density along a specific direction so that the atoms in the surface plane occupy different positions or sites from those they would in the bulk. The displacements away from the atomic positions in the bulk are small and, therefore, the compression is spread over many atomic distances (22 to be precise) (*figure 3a*).
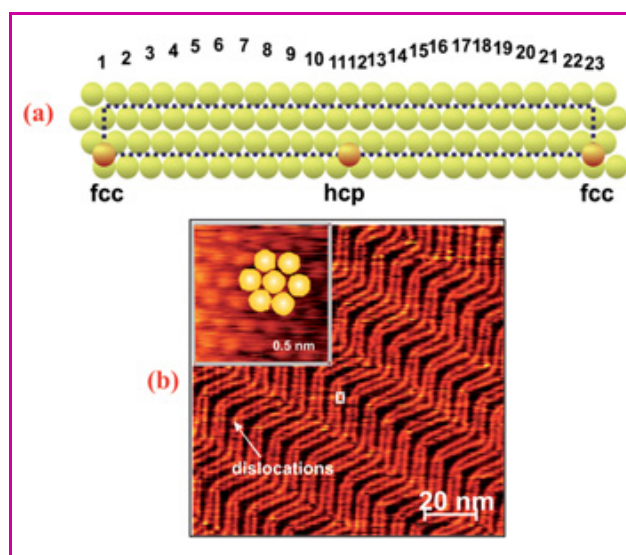

Figure 3 - A top view (a) of the Au(111) surface is shown.
The hexagonal arrangement of Au atoms is the arrangement in the bulk. When the surface is formed, the structure is distorted and extra atoms (available from step defects in the surface) are incorporated so that the surface atoms are compressed along the horizontal direction shown. The orange balls show the positions of selected Au atoms in the surface. They are only in the same position as the bulk termination every 22 atoms. In between, the atoms are slightly displaced from the triangular structure. The different spacing of atoms in the top layer net compared to those underneath creates a Morire' pattern that manifests itself as stripes in the STM image (b) shown below. The direction of the compression changes periodically so as to relieve the strain in the layer, leading to the characteristic herringbone pattern shown. The surface itself is not completely flat on an atomic scale. The numbers above the top schematic denote the atoms in the repeating unit shown and schematically show how the height of these atoms varies across the surface. The STM image (b) shows two different length scales: the larger scale shows the complex herringbone pattern and the inset shows the individual Au atoms in the structure. (figure provided by Dr. Weiwei Gao).

The displacement of atoms relative to the bulk leads to an interference or Moire' pattern that is manifested in the STM image obtained for this surface. This interference pattern is analogous to superimposing two screens with slightly different mesh sizes so that they create an interference pattern. In the case of the STM image, the bright and dark stripes are due to interference in the electrons associated with the Au atoms in the top and underlying layers.

As can be seen from the pattern in the STM image, the interference pattern makes twists and turns across the surface. The turns in the pattern reflect the fact that the direction of the compression in the surface atoms changes direction. The displacement of the atoms on the surface creates some loss of bonding to the layer below creating surface "strain". The surface relieves this strain by creating turns in the direction of the compression. The atoms at the turns, called the "elbows", are also displaced out of the surface plane very slightly in order to relieve the strain (*figure 3a*). Finally, if we zoom out and obtain a large scale image (spanning hundreds of atoms), we observe one atom high steps that are defects present at finite temperature. These steps, as noted above, are sources for atoms needed in the rearrangement of the surface. They also serve as sinks of atoms that are expelled during chemical reactions (more below).

While the rearrangement of the Au(111) is very complex, it illustrate key and rather simple points. First, atoms on the surface can and do rearrange in order to assume their most stable structure. Second, the scanning tunneling microscope can image these structural changes. Third, defects, especially atomic-scale steps, are always present to some degree on a surface. The atoms at these steps have even fewer neighboring atoms than other surface atoms and, therefore, are most easily moved around on the surface.

Why study reactions on gold?

Chemical reactions on gold surfaces are very important technologically even though we usually think of Au as being relatively inert. Gold is used in a wide variety of applications. Most commonly, we think of gold as a decorative precious medal used in, for example, jewelry. From this point of view, we need to understand the chemistry of gold extraction from ores, prevention of gold corrosion, and the plating of thin layers of gold onto many objects. Gold is also an essential component of microelectronic circuitry, on which our modern world relies. Very thin layers of gold are used to make electrical connections in microelectronic devices of all sorts, so that structural or compositional changes due to reaction with ambient molecules could lead to resistivity changes and disruption of the circuit. More recently, gold has also been shown to be catalytically active for the oxidation of carbon monoxide, a pollutant in automotive exhaust and other combustion sources, and hydrocarbons to make important synthetic building blocks [5]. The variety of applications that rely on gold surface chemistry makes this a fascinating material to investigate.

Seeing surfaces change during the reaction of SO_2 on gold

The favored structure of a surface is a delicate balance of forces that can be disrupted by reactive gases. The herringbone structure of Au is favored when the surface is clean, exposed only to vacuum, and allowed to reach its most stable state in a temperature range around room temperature. Reactive species that bind to the gold surface can change the

favored arrangement of atoms on the surface and also facilitate the rate at which atoms can move on the surface. We have found that the structure of the gold herringbone is transformed when electronegative atoms – atoms that strongly bind electrons, such as chlorine, oxygen and sulfur – lead to expulsion of atoms from the surface and a substantial change in the surface structure [6-7]. At the same time, the participation of gold atoms, including their release or incorporation into the surface, contributes to the reaction energies and the rate. Both the energy and the entropy of reaction can be strongly affected by the loss of Au-Au bonding and the increase in entropy due to disordering of the surface. These key points are illustrated below by examples derived from our recent work.

Our studies of sulfur deposition during reaction of SO_2 on Au provide a clear illustration of changes in the Au surface during reaction [7-9]. The formation of Au-S layers is important in several technologies, including corrosion of gold, especially in microelectronic circuitry, formation of self-assembled monolayers used for lithography [10-12], formation of gold ore [13] and possible deactivation of gold-based catalysts. Besides the importance of the Au-S interaction, this example illustrates a general phenomenon: that atoms on many solid surface move extensively during reaction and, indeed, participate in the reactive process in a way not envisioned prior to our ability to image surfaces.

In the case of SO_2 reaction on the Au(111) herringbone surface, sulfur atoms are deposited and oxygen is carried away by subsequent reaction with a second SO_2 molecule. The rate of sulfur build up on the surface is monitored independently using a tool for measuring the composition of the surface called Auger electron spectroscopy. This same experiment shows that no oxygen remains on the surface during SO_2 reaction. We were able to monitor the surface structure *in situ* during SO_2 reaction which leads to S deposition and formation of gaseous SO_3 so that only sulfur builds up on the surface.

Changes in the surface structure induced by reactive deposition of sulfur is shown by snapshots of the surface obtained using our scanning tunneling microscope (*figure 4*). The images shown were obtained during the reaction of SO_2 with the Au(111)-herringbone surface at room temperature (300 K). Two different length scales are shown to illustrate the changes in structure on both an atomic scale and on a larger scale that shows global changes. The first panel is the pristine herringbone structure which is visible in the inset at higher magnification. The larger image shows that there are some one-atom high steps on the surface which, notably, have rather straight, well-defined edges. These characteristics show that the surface is in a stable state that minimizes the surface tension (surface free energy).

As sulfur is deposited on the surface from reaction, Au is drawn out of the surface to form mobile Au-S complexes. At first, this effect is manifested by a disruption of the herringbone structure so that it is somewhat disordered and by a change in the step edges so that they are wavy (*figure 4b*). The wavy steps are due to the fact that Au released from the surface migrates across the flat regions of the surface and bind to the steps. Because the surface temperature is rather low (room temperature), the atoms take some time to rearrange and, therefore, do not immediately organize into straight step edges, which are the more favorable configuration. The loss of some Au atoms from the original herringbone pattern disrupts the packing of the Au and changes the Moiré pattern.

Ultimately, a two-dimensional layer of AuS precipitates on the surface and the reaction stops because this layer is inert to reaction (*figure 4f*). The AuS layer that forms at room
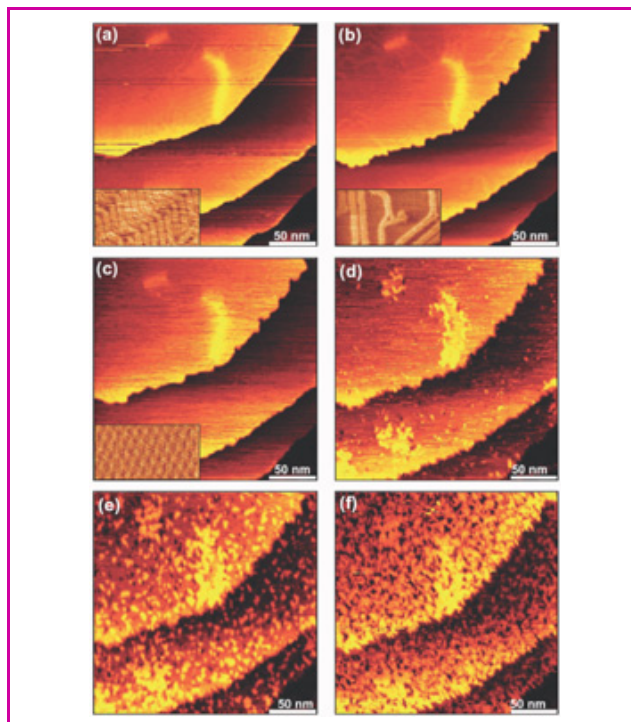
Figure 4 - Scanning tunneling microscope (STM) images showing structural changes in Au(111) surface due to release of Au atoms from the surface into a mobile Au-S complex.
(a) Clean Au(111) showing herringbone reconstruction (see inset 90 nm × 50 nm); (b) Early stages of S deposition include disorder in the herringbone as Au is released (inset 75 nm × 40 nm) and development of irregular step edges due to migration of Au-S complexes; (c) Mobile Au-S complexes skate on Au(111) where the herringbone is completely absent and Au atoms are resolved (inset); (d-f) A granular, two-dimensional AuS layer forms on top of the Au surface that contains released Au atoms at which point the reaction ceases. All images were obtained in real-time during the course of reaction at room temperature (300 K).
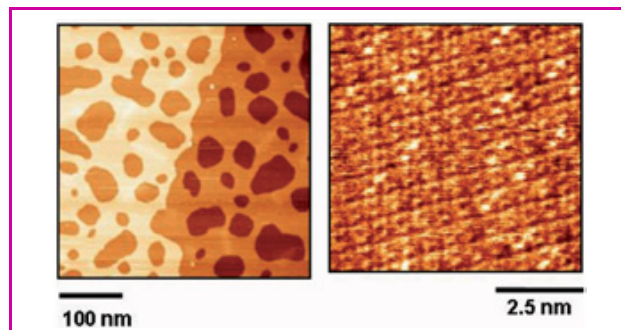

Figure 5 - The AuS overlayer orders upon heating to 450 K for ~ 20 minutes.
Scanning tunneling microscopy images are shown at two different levels of magnification. The right image shows the atom-scale ordering of the AuS layer across a large region. The image on the left shows that the surface forms a complex morphology with holes that are on the order of 50-100 nm in diameter.
The atomic ordering is the same on all areas of the surface – both in the holes (dark regions) and the upper regions. The complex morphology is attributed to a release of strain on the surface that develops because the atomic-scale structure of the AuS layer on top is incommensurate (i.e. it does not match up) with the underlying Au structure. The mismatch of the AuS and Au is confirmed by diffraction measurements and theoretical calculations.
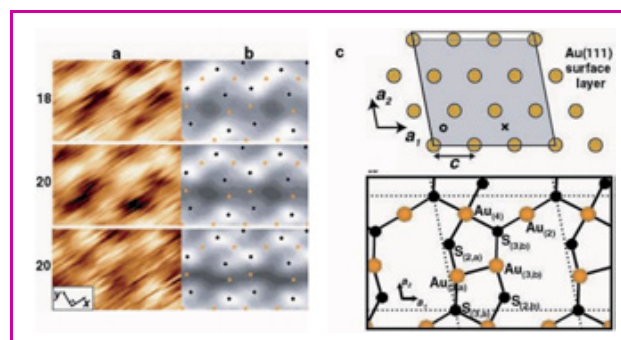

Figure 6 - The atomic scale structure of the two-dimensional AuS layer on Au(111) was determined using density functional theory (right) revealing bonding motifs similar to those found in gold oxide compounds.
The ring-like structure is similar to compounds with Au in the +2 oxidation state. The 2-and 3-fold coordination of S is similar to O in Au_2O_3 and indicate that Au^+ and Au^{3+} are also present. On the left, (a) experimental STM images at high magnification are compared to (b) simulated images to validate the theoretical structure. (Figures are used with permission).

temperature (300 K) is granular, i.e. not ordered over a large area of the surface, because the atoms in the layer do not have sufficient kinetic energy at this temperature to assume their equilibrium structure. Thus, exposure of circuitry containing Au to an ambient of sulfur-containing molecules, would corrode, for example. Upon heating to 450 K, the AuS layer orders so that an atomically-ordered arrangement is formed over a large area of the surface (*figure 5*). The AuS layer on top "floats" on top of the underlying Au in that there is no rational relationship between the spacing of gold atoms in the plane below and those in the AuS layer on top. The so-called incommensurate AuS layer, therefore, breaks up into smaller domains which are manifested by an arrangement of holes (darker regions) on the surface; yet the same atomic AuS arrangement is present in the holes and on the other areas of the surface. Theoretical models of surface strain predict that strain can be relieved by formation of domains such as these [14].

In order to fully visualize the bonding and structure of the AuS layer as Prof. Dubois would have, we need to employ theoretical calculations to relate the STM images to atomic coordinates. The atomic scale structure of the AuS layer shown in *figure 6* was determined on the basis of electronic structure calculations using density functional theory (DFT) [8]. The experimental STM images were simulated using the theoretical calculations in order to confirm the validity of the atomic scale structure determined theoretically. The atomic-scale structure of the AuS layer has a rich coordination che-

mistry that is analogous to some known compounds. Gold atoms are present in the layer in three different formal oxidation states + 1, + 2 and + 3. There are also two distinct types of sulfur binding in 2- and 3-fold coordinate sites.

The example of sulfur deposition on Au(111) during SO_2 reaction illustrates how metal atoms, in this case gold, participate and are very active in the reactive process. Clearly, any description of the kinetics or energetics for this reaction must account for changes in the bonding associated with release of Au atoms from the surface.

Movement of surface atoms is general in many reactions

While we have used the specific case of sulfur deposition during SO_2 reaction on Au to illustrate how dynamic surfaces are during a chemical reaction, the effect we describe is quite general. Gold atoms are released from the surface into mobile complexes in several other reactions on the (111) herringbone surface, such as CO oxidation [15] and formation of a chlorine

layer from reaction of Cl_2 (unpublished results). In the case of CO oxidation, the specific arrangement – both atomic-scale and over larger length scales – is important in determining the kinetics of reaction [15].

Chemical reactions on other materials, e.g. copper [16], silver [17] and nickel [18], also lead to significant changes in the structure of the surface that pull atoms out of the surface in order to make a complex bound to the surface. Other examples are sure to follow as chemical reactions on a wider range of materials are investigated using imaging techniques. Thus, the dynamic behavior of surface atoms is not limited to gold.

Summary

The ability to image surfaces during chemical reaction and to understand structural and bonding changes on surfaces at an atomic scale using advanced theoretical methods has revolutionized our thinking about this important class of chemical reactions. Clearly, surfaces are dynamic entities even though they appear immutable to the eye. Importantly, the bonding of atoms in the surface can change dramatically during the course of a chemical reaction. The changes in bonding of surface atoms during the course of a reaction must be taken into account in modeling of kinetics of important chemical processes that occur on surfaces. The insight we gain from these studies further suggests principles for the design of materials with different functions in mind. In some applications, i.e. formation of thin films for microelectronics, we may want to inhibit reactions and design surfaces that are inert. For other applications, i.e. catalytic oxidation reactions, we may design catalysts that have readily movable atoms. Finally, the new technology and understanding we have gained open new avenues for manipulation of matter at very small length scales important in nanotechnology.

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