Doctoral Thesis

Model catalysis and nanotechnology
advantages and disadvantages of active surfaces created by
lithography

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Model Catalysis and Nanotechnology: 
Advantages and Disadvantages of Active Surfaces 
Created by Lithography

A dissertation submitted to the
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Summary

In this study we developed, characterized, and tested supported model catalysts. The primary goal was to obtain stable systems that closely resemble industrial heterogeneous catalysts and are accessible to surface science methods. Large and well-ordered arrays of submicrometer-sized metal particles on atomically flat substrates were created by means of lithography. The surfaces of oxidized silicon wafers were structured before depositing the metal in order to increase the stability of the systems against sintering. Laser interference lithography was the method of choice to create the patterns that are required for structuring the wafers. The technique takes only a few minutes and results in $10^9$ to $10^{10}$ pits of submicrometer size and spacing, which cover a 4 inch wafer. Controlled deposition of palladium and silver into the pits by evaporation through the patterned resist as well as wet chemical impregnation by spin-coating of copper and palladium precursor solutions led to perfectly ordered arrays of metal clusters with predictable sizes.

The nanostructured model catalysts were investigated by means of scanning force microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. Topics of interest were the topography (structure and arrangement) and the chemical composition (chemical state and number of impurities) of the active metal clusters on the pitted surface after the synthesis as well as changes, that were induced by the reaction conditions in, for example, stability and chemical behavior. Analysis of the reaction products of model reactions (oxidation of carbon monoxide and hydrogen) was performed using high-pressure quadrupole mass spectrometry.

The pitted support wafers, filled with metal by evaporation, exhibited disk-like metal films at the bottoms of the depressions after the production. These films restructured to spherical particles by annealing above 500°C in UHV or reactive gas atmosphere. The initially flat films reshaped to hemispherical particles, but no sintering was observed, even after treating the samples at 400°C and 600°C in oxygen and hydrogen. Loss of material as a result of the evaporation of volatile SiO or of diffusion of metal into the silicon bulk was prevented by thick interface layers of silica. The size of the metal spheres was controlled by varying the initial thickness of
the metallic layer. We started with deposited films, 20 nm thick; the annealed particles were typically 45 nm high and about 200 nm in diameter. Evaporation of smaller amounts of material led to smaller clusters, as was shown in the case of silver deposition.

The spin-coating of metal salt solutions on a rotating wafer was a second method for impregnating the structured substrates. The samples were calcined and reduced after deposition of the metal salts, according to the synthesis of actual catalysts. This resulted in a metal cluster arrangement of single copper particles, with typical diameters of 80 nm and 10 nm high, at the bottom of the pits. The cause of the ordered arrangement was due to the modification of the topography and the chemical properties of the surface by wet chemical etching. The method was more appropriate for producing systems with weak metal-support interactions such as the Cu/Si\(_2\)O\(_2\) system.

Oxidation and reduction cycles, as used in industrial catalysis, are appropriate for cleaning the pitted model catalysts of large amounts of carbon-containing species. These contaminations are parts of the photoresist that were left after the lithographic production process. The pitted samples were very stable in oxidizing atmospheres at elevated temperatures, even at atmospheric pressure. After cleaning and activation by the oxidation/reduction treatments, the catalysts (with evaporated Pd) were catalytically active towards the oxidation of hydrogen and carbon monoxide. The activation and cleaning treatments as well as the test reactions were carried out in a specially designed quartz glass reactor. The catalysts provided sufficient metal surface area for reaction studies, even at atmospheric pressure.
Zusammenfassung


Eine Umstrukturierung der nach der Bedampfung am Boden der Aetzlöcher vorliegenden Metallscheibchen zu kugelförmigen Partikeln wurde nach Tempern über $500^\circ C$ unter Ultrahochvakuum-Bedingung und in verschiedenen Gasatmosphären


1. An introduction to the development of modern model catalysts

1.1 Developing advanced model catalysts

Due to the complexity of heterogeneous metal catalysts, it is necessary to develop simplified model systems for basic catalyst research. Despite this, however, these models should resemble industrial catalysts as closely as possible, in order to obtain relevant data about actual processes. Catalysts used in industry usually consist of porous, insulating oxide supports, covered to a small extent (about 1%) by nanometer-sized metal particles and, possibly, by an even smaller amount of promoter materials (usually less than 1%) [Tho97]. In contrast to these highly complex systems, the model systems must be more accessible to modern characterization methods than is usual for powdered samples. On actual catalysts, the active material is hidden inside the pores of the insulating support (Figure 1-1a); thus the application of surface sensitive techniques, such as scanning tunneling microscopy (STM), scanning force microscopy (AFM), secondary ion mass spectrometry (SIMS), X-ray photoelectron and Auger electron spectroscopy (XPS, AES), etc., is often impossible. In some cases, exploiting the full potential of these methods is hindered.
by a loss of intensity and resolution.

Therefore, metal single crystals, metal foils or flat oxidic supports, covered with metal films or particles, have generally been applied as model catalyst systems thus far. Single crystals (Figure 1-1b) and metal foils have been used successfully to identify some of the important steps and reaction pathways of catalytic reactions [Som94] as well as to investigate the mechanisms involved in the reconstruction of metal catalysts due to thermal or catalytic etching [Wei96]. Therefore, the general importance of surface science studies for the development of catalysts in heterogeneous catalysis is widely accepted [Bha99].

However, single crystals and metal foils are one-component systems that are very different to supported heterogeneous catalysts. The large number of publications on the production and testing of "model catalysts by design" (Figure 1-1c) underlines the necessity for more "realistic" catalyst systems. Gunter et al. [Gun97] and Henry [Hen98] presented comprehensive surveys of a variety of model systems for heterogeneous catalysis. According to these reviews, evaporated films of catalytically active metals on flat substrates are still frequently used in surface science studies of heterogeneous catalysis. These catalysts are often prepared on flat substrates made of oxidic material or on slightly oxidized metal substrates, and are more similar to industrially used catalysts than are single crystals or polycrystalline foils.

When very thick metal films (up to a few hundred nanometer) are deposited, the resulting systems are close to the single crystal or metal foil systems. In general, however, thin metal layers (sub-monolayers up to a few nanometer thick), created on oxide surfaces by evaporation under vacuum conditions, are used. Subsequent vacuum annealing leads to isolated particles on the support. The size and arrangement of the particles strongly depend on the nature of the support, the metal, and on the conditions of evaporation and annealing. The resulting particles usually vary considerably in size, and the arrangement is quite irregular.

Since small metal particles on a flat oxide support resemble industrial catalysts, a substantial effort has been made to improve the deposition of well-defined metal clusters onto flat surfaces. For this purpose, various methods are available for producing and stabilizing particles of the desired size in solution before impregnation [Wit96], [Che98]. To deposit particles under vacuum, evaporated metal clusters can
be selected according to size in the gas phase [Hei99]. The size distribution of the metal particles on these systems is quite narrow unless the systems are treated at high temperatures and in reactive gas atmospheres. However, in addition to the precise control of the size, the control of the spacing between the individual particles is highly desirable. Furthermore, the model system should exhibit defined contact areas between the support, as well as between the metal and the promoter materials. For tests under catalytic conditions, high stability at elevated temperatures and under reactive conditions is essential. For sufficient signal to noise ratios, large surface areas of catalytically active material are necessary. The ideal production method must, therefore, deliver large numbers of these ideal systems in a short period of time and at low expense.

1.2 Lithography as a tool for the production of model catalysts

1.2.1 Photolithography and electron-beam lithography

Many attempts have been made to meet at least some of the requirements mentioned above. Nevertheless, it seemed just about impossible to fulfil the innumerable demands on an ideal heterogeneous model catalyst. It has to be stressed that any technique must meet at least two requirements, which are, however, somewhat contradictory. The first requirement is to produce predictable and variable particle sizes from some Ångstroms to a few nanometers. Since it is possible to manipulate and arrange even single atoms on surfaces (for example: iron atoms on a Cu(111) surface [Cro93]), this requirement can be fulfilled technically. However, since it takes minutes to build only one such quantum array, and a tremendous number of identical particles must be produced in short periods of time; therefore, parallel production methods are highly desirable. Recent developments in the modern microelectronic industry are aiming to fulfill the same requirements: cheap and fast production of submicrometer-sized circuits. Although the present dimensions of the features in computer chip production are still too big to be compared directly to particle sizes required of most heterogeneous catalysts, further developments will bridge this gap.
In 1986, a lithographic fabrication sequence was used to produce "slotted microstructures" [Dec86], [Rox86]. Amorphous superlattices made of alternating layers (1 – 3 nm thick) of hydrogenated amorphous silicon and silicon oxide, silicon oxide and silicon nitride, as well as silicon and germanium were produced by plasma-assisted chemical vapor deposition [Dec85], [Per85]. Wet chemical etching of the layers gave slots with high aspect ratios perpendicular to the surface. Adsorption of organic molecules in these slots was carried out to test the microfabricated structures for use in shape-selective adsorption and for chemical reactions similar to those in zeolites. To the best of our knowledge, this was the first combination of microstructures produced by lithography and experiments in the field of catalysis.

Six years later, lithography was introduced as a method for creating well-ordered structures in the field of heterogeneous model catalyst research by Saltsburg and Zuburtikudis [Zub92]. At that time, conventional photolithography was used for building "layered synthetic microstructures" (LSMs), which consisted of forests of micrometer-sized towers on top of an oxidized 3 inch wafer. In this context, conventional means that pre-produced square-patterned masks were applied for the selective exposure of the photosensitive resist material. Multi-layered systems of alternating nickel and silicon oxide films were produced by electron beam evaporation, followed by photolithography and subsequent wet-chemical etching. The resulting individual towers had diameters in the micrometer range or greater, whereas metal catalysts in the form of strips (2 – 10 nm) were exposed at the side-walls of the towers. The catalyst systems have been used to investigate size effects in the hydro-

![Figure 1-2](image_url)

**Figure 1-2**
SEM image of a “Nanotower” sample. Partially etched towers (c) are visible on unetched multi-layers (b) and the supporting wafer (a). Since the etching was interrupted, remaining resist material (d) sits in form of caps on top of the towers. By kind permission of Y. Bonetti.
genolysis of ethane. LSMs with a wider range of metals (Ni, Pt, Ir, Rh, Ru) and supports (SiO$_2$ and Al$_2$O$_3$) were produced fairly recently in the research group of Saltsburg [Cha97], [Lu97]. Laser interference lithography was used to create comparable systems on 4 inch wafers by Bonetti [Bon00]. Figure 1-2 shows an electron microscopy image of a partially etched system and gives a good impression of the steps involved in the complete process of creating high aspect ratio features by lithography. The "Nanotowers" model catalyst system was produced by sputter etching of a number of bilayers (palladium/silicon oxide), stacked on an oxidized Si wafer surface. The etching mask was produced by laser interference lithography (which will be described below, see Chapter 3) in a photosensitive resist material, spun on the multilayer sandwich of Pd/SiO$_2$. From bottom to top, the oxidized wafer (a), unetched multilayers (b), partially etched "towers" (c), and a "forest" of resist caps (d) are distinguishable in Figure 1-2.

The etching results in billions of isolated towers, consisting of disks of active metal layers, separated by inert substrate material. Two examples of such towers are presented in the transmission electron microscopy image of Figure 1-3 (image recorded by E. Müller, Institute for Electron Microscopy, ETH Zürich). They consist of 40 bilayers, the alternating metal and insulator layers being about 3 to 10 nm thick. The diameter of the towers is about 200 nm, and they range in height from 300 to 600 nm. Sputter deposition was used to deposit the multi-layered material onto the wafer. The active species is present as the rims of the metal disks that make up the towers.

Two years after the publication of Zuburtikudis and Saltsburg, Krauth et al. presented a much simpler system [Kra94]. Arrays of well-ordered Pt particles with diameters of about 5 μm on an oxidized Si wafer were produced by means of con-
ventional photoresist techniques. Applying techniques used in the microelectronics industry for miniaturization of circuits, well-ordered arrays of metal particles, with diameters as small as 20 nm, can be produced today by e-beam lithography [Jac96], [Jac97], [Yan97], [Yan98], [Joh99]. These systems have a number of excellent features (well defined, separated, nanometer-sized metal clusters, easy accessibility by surface science methods, high reproducibility), but serious problems remain to be solved. Not only is e-beam lithography in particular an expensive and time-consuming technique when a large number of metal dots is required on a support surface, but removing the resist material after metal evaporation ("lift-off") commonly leads to a surface contaminated by large amounts of carbonaceous species. Therefore, the poisoned catalyst is fairly inactive and unsuitable for the purpose it was intended for. Thus far, most of the cleaning techniques used in surface science are not satisfactory. Sputtering leads to systems that are not as well defined due to the roughening of the surface. Furthermore, spreading the active material over the substrate and redeposition of sputtered material must be taken into account. Cleaning the catalysts in oxygen plasma can cause the support material to migrate over the metal particles [Jac96]. Burning the carbon contaminations in an oxygen atmosphere at high temperature is often hindered by the instability of the systems under oxidizing conditions. Therefore, only few reactions, such as hydrocarbon hydrogenolysis and hydrogenation ([Zub92], [Kra94], [Kra97], [Jac97]) as well as hydrogen oxidation [Joh99], carried out on such models have been reported (most of the investigations were carried out under reducing conditions).

1.2.2 Nanosphere lithography

An alternative method for transferring a pattern from an imaging layer to a device or structure is the use of so-called “nanosphere lithography“ [Hul95], [Hul99], [Jen99] or “colloid monolayer lithography“ [Bur99] (see also [Dob95], [Du98], and references therein). This technique is based on the principle of a self-organized assembling of colloidal particles (usually polystyrene spheres) into a two-dimensional array on flat surfaces. A highly ordered film of monodispersed polymer spheres is prepared by different techniques including spin-coating, electrophoresis, the Langmuir-Blodgett method, and others. The 2D crystals, consisting of one or two layers of hexagonally
close-packed spheres, can be used as lithographic masks for consecutive processes like evaporation of metals. If the polymeric film is dissolved away after the metal evaporation, metal features are located on the surface, where the interstitial spaces between the densely packed spheres had been. The schematic diagrams in Figure 1-4 show the production routine and a projection of the holes (created by the interstitial spaces between the spheres) on a surface (black) created by a single layer sphere mask (white spheres) and a second layer (grey spheres) on top of the first layer. The scanning force microscopy image in Figure 1-4 shows the topography of a sample, prepared by colloid spheres lithography (by a double layer sphere mask). The sample was prepared by F. Burmeister (Prof. Dr. P. Leiderer, University of Konstanz, Germany) and investigated in our laboratory. The polystyrene spheres used in this experiment had a diameter of 300 nm. As can be seen in the micrograph, a number of defects can be found even on small scan areas. According to [Hul99], defect-free areas of up to 25 μm² can be produced. To the best of our knowledge, no catalytic investigations have been carried out thus far on such systems.

**Figure 1-4**

Preparation scheme of nanosphere lithography and AFM image of actual sample (4 x 4 μm²).
1.2.3 Limitations of the lithographic procedures and outline of a new approach

All methods that include the evaporation of metal and a lift-off step, have the disadvantage that the lift-off procedure is wasteful as far as expensive noble metal films are concerned and that the evaporation of the metals under high vacuum conditions is not necessarily comparable to the typical wet chemical impregnation techniques used in catalysis. This cannot be overlooked, since structure, morphology, and catalytic properties are often strongly influenced by the methods of preparation.

In conclusion, the advantages and disadvantages of catalyst systems produced by lithography can be summarized as follows: the well-ordered arrangement of a number of nearly identical structures on a flat surface is easy to realize. However, the particles, which can now be produced with modern equipment, are still far too large and are contaminated by the reactants used during production processes. The use of evaporation or sputtering techniques for the deposition of metal particles is not comparable to wet chemical impregnation methods and the systems thus produced are not sufficiently stable to withstand harsh catalytic conditions.

In this study, the development of well-defined systems that are stable enough to withstand sintering processes is reported. To achieve this, the formerly flat surfaces of oxidized silicon wafers were structured by the use of laser interference lithography and wet chemical etching of pits. The method is capable of fast and convenient production of model catalyst systems with submicrometer sized features on 4 inch wafers at low expenses. The resulting models mimicked porous substrates. Due to their stability the applying of cleaning procedures used in actual catalysis were tested to remove carbonaceous adlayers from the surface. One approach towards creating an ideal model catalyst system was to combine the lithographic procedures with methods of impregnation used in industrial catalysis. This will be described in the next section.
1.3 The combination of lithography and spin-coating

A method for producing defined model catalyst systems, similar to methods used in the industrial manufacture of catalysts, is the spin-coating of inorganic precursor solutions onto flat substrates, first tested by Kuipers et al. [Kui93a], [Kui93b]. The metal salt solution is dropped onto the sample substrate (usually a piece of an oxidized silicon wafer) that is mounted on the axis of a spin-coater. Starting the rotation leads to the spreading of the solution over the surface due to the centrifugal force and to a thin liquid layer on the wafer. Shortly after the start of the rotation, most of the solution is flung from the wafer and the liquid loss due to evaporation is the dominant process (Figure 1-5). Calcination (followed by reduction) of the resulting metal salt films leads to metal oxide or metal clusters on the substrate. The amount of deposited material and the size of the particles are influenced by various parameters, such as the concentration of the solution, the rotational speed, the partial pressure of the solvent above the rotating substrate, and the heating parameters. A number of publications about the experimental [Doo95], [Wij97] as well as the theoretical [Har95] aspects of this technique has been published in recent years. Detailed investigations of the support/metal interactions of different metal/support systems prepared by spin-coating, such as rhodium and copper on SiO₂ [Par96], cobalt and molybdenum on SiO₂ and Al₂O₃ [Jon97], and CuO on SiO₂ (see [Bro99], [Chu99], [Oet98a], and [Oet98b]), and of working catalysts for the polymerization of ethylene have been reported [Nie99], [Thü98], [Thii99]. Platinum particles have been immobilized on silicon oxide surfaces by spin-coating with colloidal solutions [Che98]. According to these publications, the amount of deposited material and the size of the particles are each dependent on the spin-coating parameters and can be controlled exactly.
The efficient and cheap production of high-surface area catalysts (compared to e-beam based methods) is a major advantage of this method. However, homogeneity of metal cluster size and the arrangement of the particles on the surface are also strongly influenced by impurities such as dust or moisture on the silica surfaces. Intense sintering of the metal clusters due to poor anchoring on atomically flat surfaces occurs in oxidizing gas atmospheres at high temperatures, regardless of the chosen method of production.

The use of a flat but structured surface of an oxidized silicon wafer as a base for metal deposition by spin-coating was thought to lead to model catalysts comparable to the systems introduced by Kuipers. The idea was to improve the regular arrangement of the deposited metal material and to increase the stability of the resulting systems by the well-ordered structures on the substrate surface.

1.4 The aim of this work

Methods for producing model catalysts that combine most of the advantages of the various techniques described above are reported here. The aim was to develop a method for building active catalytic systems that nearly reach the particle dimensions and have the same well-defined arrangement of particles as models produced by e-beam lithography. At the same time, they should be considerably more stable, even at high temperatures, should be capable of producing larger amounts in a shorter period of time, and should be much less expensive. We used laser interference lithography and wet-chemical etching for the nanostructuring of an oxidized 4 inch Si wafer surface. The resulting model support mimicks porous support materials and consists of about $10^9$ to $10^{10}$ nanometer-sized pits in the flat SiO$_2$ plane of a 4 inch
wafer. The structured surface was used as a base for metal deposition by evaporation or wet-chemical impregnation (spin-coating). The resulting model catalysts exhibit well-ordered clusters of metal or precursor species right inside the pits. Size and chemical composition of the active material could be influenced by subsequent heating and oxidation/reduction treatments. Because of the immobilization of the metal or metal salts inside the pits, their original arrangement on the surface was maintained even at high temperatures, in pure oxygen, and in humid atmospheres (tested up to 800°C). This led to the possibility of investigating the behavior of isolated metal particles on supported catalyst systems.

Furthermore, the chemical and topographical behavior of a pure bulk sample (foil) was compared to the behavior of the model catalyst under the same catalytic conditions. The probability of a single atom, initially located in the bulk of a very small metal cluster, being exposed to the surface as a result of restructuring processes during a catalytic reaction is significantly higher than for a single atom in a larger particle. This may play an important role in the catalytic performance of multi-component particles such as alloys, where the ratio of the various species on the surface is essential for the properties of the system. Phenomena such as sintering, redispersion, and changes in the particle shape of catalysts, induced by processes such as thermal and catalytic etching, [Wei96] were investigated in the past in detail using important catalytic metals (e.g., silver, copper, platinum, and rhodium). In semiconductor research, emphasis has been placed on elements such as silicon, aluminum, and titanium [Bec93]. There has been little, if any, cross-referencing between the two research fields. To the best of our knowledge, little has been published on palladium-based systems.

It is usually difficult to compare results obtained with model systems in catalysis and surface science, because the results are influenced by the methods of preparation, the quality and the purity of the materials used, as well as by the technical equipment. Carbon and other contaminants strongly influence the equilibrium shape of supported metal particles, as known from Pt catalysts [Wei96]. Therefore, with the exception of the foil sample, all the model catalysts in this study were prepared as far as possible on identically prepared substrates with the same parameters.
1.5 The outline of this thesis

This introduction will be followed by an overview of the experimental methods used for the characterization and the manufacture of the catalytic systems. Therefore, Chapter 2 describes of the common principles of the methods and of the experimental set-up. Chapter 3 gives the basic steps in the production of the model catalysts by laser interference lithography.

The experimental part is followed by three chapters which are based on the results and the conclusions of three refereed papers (Catalysis Letters, [Sch98], Topics in Catalysis, [Sch99a], Journal of Physical Chemistry B, [Sch99b]). Chapter 4 and Chapter 5 describe the preparation and the properties of the nanostructured model catalyst systems, whereas in Chapter 6 a comparison of chemical and topographical behavior of these new systems and standard, non-structured model catalysts (metal foils and evaporated films) is given. Each chapter concludes with comments on the reported investigations and unpublished results, which may be helpful in understanding the possibilities and limitations of the described models. Chapter 7 gives a more detailed description of the production and the properties of nanostructured silver catalysts.

The conclusionary remarks and the perspectives will summarize the results obtained so far as well as future challenges in this field.
2. Experimental: analytical methods and equipment

2.1 Introduction

Heterogeneous catalysis is a research field with a need for expertise in many different disciplines. Knowledge of organic and inorganic chemistry, surface and solid state physics, as well as material science and engineering is necessary, to understand the multiple facets of catalysis. A variety of methods are available today to obtain data on catalytic activity, selectivity, and the bulk and surface properties of catalysts. The number of analytical tools used in catalysis research has strongly increased since the rapid development of surface-sensitive methods as, for example, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Such methods were used initially to investigate the basic principles of catalysis on single crystals or metal foils but were soon adapted and widely accepted for the analysis of supported catalyst systems.

Today suitable analytical methods or a combination of methods are available to solve many of the problems related to the appearance and performance of a heterogeneous catalyst.

The aim of this section is to categorize the main analytical methods that were used in this work. Atomic force microscopy (AFM), scanning electron microscopy (SEM), XPS, and quadrupole mass spectrometry (QMS) will be introduced and the main principles will be explained. Since the techniques are well known, a detailed explanation will not be given here and the reader is referred to the literature where needed. The set-up and modifications made to the equipment as well as common difficulties that may be encountered in the application of these methods will be described.

Furthermore, a short overview will present the different types of model reactors that were built and tested for the catalytic investigations of the catalyst systems described here.
2.2 Atomic force microscopy (AFM)

2.2.1 General principle of the method

Since its invention in 1986 [Bin86], atomic force microscopy has become one of the most widely used scanning probe microscopy techniques. A variety of commercial equipment is available for use under vacuum or in ambient conditions. Compared to related techniques like scanning tunneling microscopy (STM) or scanning nearfield optical microscopy (SNOM), AFM offers a number of advantages. Easy handling of the computerized machines and a variety of high quality cantilevers and tips of various geometry allow the convenient and fast investigation of almost all flat samples. Since different techniques are usually combined in a single piece of equipment, a variety of information (topography, elasticity, lateral forces between the sample and the tip, magnetic forces, etc.) can be obtained; some simultaneously in a single scan. AFM is now commonly used in industry, especially in semiconductor industry and companies that produce data storage [Pfa99]. While one of the original aims related to the invention of the microscope was to achieve atomic resolution on insulating samples, the equipment is now used mainly for imaging large areas (some 100 μm²) with excellent z (height) resolution.

2.2.2 The Autoprobe CP microscope

In this study, an “Autoprobe CP” (ThermoMicroscopes, former Park Scientific Instruments) was used. The system is equipped with scanners for a maximum scanning range of 144 μm² and microscope heads for imaging samples in contact, non-contact, intermittent-contact, and lateral-force mode. In contact-mode, also known as repulsive mode, the AFM tip makes physical contact with the sample. As the scanner traces the sample under the tip, the contact force causes the cantilever that holds the tip to bend due to changes in topography. The bending of the cantilever is detected by an optical system, and the computer system of the AFM generates the topographic data set.

The non-contact and intermittent-contact modes are vibrating cantilever techniques. A cantilever is vibrated at frequencies of 100 to 400 kHz near the surface
of the sample (some tens to hundreds of Ångströms). Depending on the exact distance between the tip and the sample surface, the tip hits (or “taps”) the surface at the bottom of its path (intermittent) or does not make contact with the sample at all (non-contact). In both cases, changes in the resonant frequencies of the cantilevers, which reflect changes in the tip-to-sample spacing (i.e., topography of the sample), are detected by the same optical system used in contact-mode and are used to generate the data set. Intermittent and especially non-contact AFM can produce sample topography measurements with little or no contact and, therefore, with only slight lateral force between the tip and the sample. In the case of very soft or elastic samples (polymers, organic adlayers), this prevents tip-induced changes in topography. On the other hand, in the case of hard materials, imaging is not negatively affected by tip degradation. In many cases, however, taking an intermittent or non-contact AFM image requires more expertise than working in the contact-mode. The vibrational techniques are much more sensitive to noisy environments, and even a few monolayers of adsorbed water on the surface of an investigated sample may change the appearance of the image.

Lateral force microscopy (LFM) is used to image variations in surface friction that can arise from various materials on the surface. It measures lateral deflections (twisting) of the cantilever, while the tip is scanned (in contact mode) parallel to the surface. Since the cantilever usually twists strongly when it encounters a steep slope, the LFM mode is used mainly on very flat samples (with mono-atomic or very few steps) [Sch96]. The extreme differences in height on the samples described in this work disabled the use of LFM.

All the images shown here were recorded with a resolution of 512 x 512 data points per image; scan frequencies were between 0.5 and 5 Hz, depending on the scan area. They are presented as grey scale and as three-dimensional images, or the error signal of the feedback loop of the instrument is shown. In grey scale presentation, brightness corresponds to vertical height on the surface: the higher the points, the brighter they appear; lower points are darker. Since the possibility of presenting a scale of brightness on a monitor or by a printer is limited by the grey scale resolution of the equipment, this method of presentation gives only poor results when small features must be shown in an area of large height differences. If this is the case, then a
three-dimensional representation may help. The 3D rendering is computed by the software, based on the grey scale images. The method is based on the stacking of the individual line traces on top of each other (with the appropriate grey scale denoting height). Since the image is depicted from the front to the back of the screen (or the paper), lower features in the back are "hidden" by higher features in the front. By means of computerized effects, such as light sources aimed above the surface so that shadows are thrown by the features, the impression of height and depth of an image is enhanced. Since the microscope records the exact surface height at a grid of x and y locations, the data set of x, y, and z points represents the true surface topography. However, effects such as shadows on the surface are produced by the computer and do not represent the actual situation.

If the 3D presentation is not sufficient to reveal small features on surfaces with large differences in height, then the error signal of the feedback loop (for the z scan direction) of the microscope can be used to give an impression of the surface topography. This error signal is a measure of the distance from the tip to the sample (or a measure of the bending of the cantilever in contact mode). When this separation is at the given set point, the error signal is zero. Positive values imply a greater separation from the head to the sample, negative numbers a smaller distance. The feedback loop adjusts its output signal (which drives the piezo in the z direction) to attempt to drive the error signal to zero. Therefore, observing the error signal gives a good indication of the movement in height of the piezo. If the z error signal is recorded in grey scale presentation, an image that suggests the topography is created: scanning a flat area will result in a grey scale image with a single brightness, with elevated features appearing darker on one side of the feature (where the scanner retracts the tip from the surface in order to follow the topography), and the same features appearing brighter on the opposite side. Since images recorded in this way appear as if illuminated from one side by an artificial light source (with "shadows" on the opposite side), they suggest a three-dimensional topography. However, the image does not give actual topographical information and is useful only for visualization. The signal cannot be used for exact measurements of differences in height.

The cantilevers and their tips are the most critical components as far as quality, the resolution, and the information obtained during the measurements are concerned.
In this work, conical tips made from silicon (boron doped, specific resistance 0.001 Ωcm) with high aspect ratios were used. Typical tip radii were smaller than 10 nm. The high aspect ratio makes them suitable for imaging deep, narrow features such as trenches. On the other hand, they break more easily than the usual pyramidal or tetrahedral geometry tips. It was essential to use such tips in this study, since the lithographically produced structures on the SiO₂ surfaces also exhibited high aspect ratios. Preliminary measurements with standard pyramidal tips gave poor results. It was not possible to image the bottom of the pits of the samples described in the Results section.

The cantilevers and tips were purchased from Park Scientific Instruments (Park Ultralever™) and from NT-MDT. The Park levers are coated with a thin layer of gold for better reflectivity. Spring constants of the cantilevers used for contact measurements ranged from 0.2 to 0.4 N/m. Cantilevers with spring constants from 13 to 17 N/m were used for vibrational techniques. The NT-MDT levers had comparable parameters but were coated with aluminum and had longer tips (7 instead of 4 μm). Tips from different manufacturers revealed identical images of the same test sample. Much more important for the reliability and the quality of the recorded data was the history of the individual tip. After scanning a number of regions on a sample, the tips usually degenerated due to the interaction with the hard SiO₂ sample surface. After observing this, the same sample was usually investigated again using a new tip for comparison.

A great deal of additional information about scanning probe microscopy is available. Thermomicroscope Ltd. has published a basic introduction [PSI97], and Brune et al. (Eds.) [Bru97], Garcia et al. (Eds.) [Gar98], and Wiesendanger (Ed.) [Wie98] have written more detailed reviews of actual developments in the field of scanning probe microscope techniques.
2.3 X-ray photoelectron spectroscopy (XPS)

2.3.1 General principle of the method

XPS is one of the most frequently used techniques in catalysis [Nie95]. The method is invaluable for determining the chemical composition and the oxidation states of elements in a near-surface region of a catalyst and are, therefore, extensively described in the literature [Bri83], [Car75], [Ert85], [Gho83]. XPS is based on the photoelectric effect: an atom absorbs a photon of energy $h\nu$. If the energy of the photon is sufficiently high, a core or valence electron of the atom is ejected into the vacuum. If $E_b$ is the binding energy of the electron, then the kinetic energy $E_k$, with which the electron leaves the atom, is described as

$$E_k = h\nu - E_b - \phi$$

where $\phi$ is the work function of the spectrometer. Since various elements show specific binding energies, which are influenced by the chemical state of the atom, the chemical composition of a surface as well as the chemical state of the elements can be identified. In general, the binding energy increases with the oxidation state of the atom, because every electron in a Pd$^{2+}$ ion is attracted by the core to a greater extent, for example, than is an electron in a Pd$^{0}$ atom. The situation gets more complicated, when charging occurs due to insulating samples. Then all of the binding energies shift to higher values, since the sample is charged positively due to the departing electrons. The values then have to be corrected according to a reference value (Si 2p or C 1s signals are often used for this purpose). In this study, the Si 2p peak of the SiO$_2$ layer (produced by dry oxidation of Si (100) wafers) was used as a reference. All binding energies are reported as they were measured but are referenced to the BE charging shift of the Si 2p.

The probing depth (also referred to as the "information depth") of XPS is determined by the inelastic mean free path (IMFP) of the excited electrons in the uppermost layers of the samples and varies from 1.5 and 6 nm. Photoelectrons excited in deeper layers will lose their energy on their way to the surface and will not reach the analyzer. When determining concentrations of elements in a sample, different
probing depths for various elements must be taken into account. It is much easier to calculate the ratio between two homogeneously distributed elements $A$ and $B$ than it is to determine the absolute concentrations of the element. According to Penn [Pen76], the relation of concentrations $X_A$ and $X_B$ can be expressed as

$$\frac{X_A}{X_B} = \frac{I_a(E_a) \cdot \sigma_a(E_a) \cdot T(E_a) \cdot \lambda(E_a)}{I_b(E_b) \cdot \sigma_b(E_b) \cdot T(E_b) \cdot \lambda(E_b)}$$

with:
- $X_A, X_B$ concentration of element $A$ and $B$
- $I_a, I_b$ intensity of the photoelectron signals
- $\sigma_{A/B}$ cross section of element $A/B$
- $T$ transmission of the analyzer, and
- $\lambda$, IMFP= inelastic mean free path of the emitted electrons.

For a given analyzer the product of the cross section and transmission is constant for each element and is referred to as the sensitivity factor. Tables of such sensitivity factors are given, for example, in [Bri90]. The ratio of the concentration is then easily determined by the ratio of the peak areas, which are determined after subtracting the inelastic background.

### 2.3.2 UHV chamber and XPS equipment

The X-ray photoelectron spectroscopy experiments described in this thesis were performed in a commercial (Leybold SA) multimethod UHV chamber, described in detail elsewhere [Reb95], [Sel97]. Non-monochromated Al $K_\alpha$ (1486.6 eV) radiation at 300 W (15 kV, 20 mA) was used. A concentric hemispherical energy analyzer (CHA EA 11 MCD, Leybold Heraeus) in the on-top position of the chamber was used for electron energy analysis. All spectra were recorded with a constant pass energy of 50 eV. Data acquisition of the system was controlled by a host computer and was based on a commercial software package (SUN Sparcstation 5, SpecsLab). All spectra reported below are raw data. The SpecsLab-software was used for deconvolution and determination of the binding energy values, for peak area integration, as well as for X-ray satellites and background (Shirley) subtraction. Values of atomic sensitivity
factors (ASF), as reported in the literatures, were used for quantitative evaluation [Bri90].

All the samples mounted in the UHV equipment were about 1 x 1 cm$^2$. By means of a frame (Figure 2-1) made of stainless steel, the samples were fixed to a coolable (-180°C) and heatable (+1200°C) sample rod. A thermocouple was welded to the base plate of the sample holder. The thermocouple was in direct contact with the backside of the samples, because the samples were pressed by the upper part of the frame onto the base plate. The use of the frame-like construction kept the time of exposure to air to 2 min when the samples were transferred from the glass reactor (described later in this chapter) to the UHV equipment and back again in air. The samples were first transferred to the preparation chamber (base pressure 10$^{-7}$ Pa) of the UHV system. They can be flashed to elevated temperatures in this chamber to remove any adsorbed material from the surface of the samples before transferring them to the analysis chamber. The preparation chamber is also equipped with gas-dosing systems, a quadrupole mass spectrometer, and a sputter gun for further treatments.

### 2.4 Quadrupole mass spectrometry (QMS) at high pressure

Quadrupole mass spectrometers are commonly used for partial pressure analysis at pressures below 10$^{-2}$ Pa. Typical applications are measurement, process monitoring, and process control tasks in vacuum systems [Daw76]. If mass spectrometers are used for the gas composition analysis of systems at higher pressures, then it is necessary to reduce the pressure. Thus, the QMS is mounted to a separate HV or UHV apparatus, and small fractions of the gases to be analyzed are passed into the recipient. This can be done dis-
continuously by step-wise dosing of small portions or by continuous dosing by differentially pumping the gas through the inlet valves.

The QMS used here was a Balzers Prisma QMS 200, equipped with a Faraday detector and a Channeltron for a mass range from 1 to 200 Da. The system was mounted to a UHV chamber; the standard pressure of which was below $5 \times 10^{-7}$ Pa. The vacuum recipient was connected to the reactor system by means of a heatable capillary and a pressure reducing valve (Balzers GEV 010). A rotary pump pumped a small amount of gas from the reactor through the capillary and the gas inlet valve. A sintered filter (comparable to a frit) was mounted in the orifice inside the valve that was opened and closed by a gold sealing, which was pressed against the filter. This set-up prevents mass-dependent fractionation and changes in the percent composition of the gas mixtures to be analyzed. The capillary and the valve were heated to $100^\circ C$ during the experiments to avoid condensation of the gases on the inner walls of the stainless steel capillary and the exposed parts of the valve. The GEV 010, in combination with the capillary (1 m long, inner diameter 0.15 mm) allows the continuous gas analysis of main and trace components (concentration higher than 10 ppm) at process pressures (in the reactor) of $10^5$ Pa. The pressure in the vacuum recipient can be varied from $10^6$ Pa to 0.1 Pa.

2.5 Scanning electron microscopy (SEM)

The main advantages of scanning electron microscopy are an easy sample preparation and a wide range of magnification. The main drawback is that the SEM images provide only poor height information. In SEM, a focused electron beam is scanned over a surface, and the yield of either secondary or backscattered electrons is detected as a function of the position of the primary electron beam. Secondary electrons have low energy and originate from surface regions of the sample. Contrast is achieved by varying the orientation of the planes of the surface to the detector: regions facing the detector appear brighter (i.e., more electrons from these regions reach the detector) than regions pointing away from the detector. Backscattered electrons originate from deeper layers and reveal some information about the chemical nature and composition of the sample, because heavy elements are more
efficient scatterers and, therefore, appear brighter in the backscattered image than lighter elements.

The primary electron beam is created by heating a tungsten filament (usually in the form of a sharp tip), and the emitted electrons are accelerated by high voltage towards the sample. The beam of electrons is focussed and guided to the sample surface by electromagnetic lenses, which are also used to scan the beam over the surface. The resolution of an SEM is dependent on the diameter of the beam on the sample and is usually around 10 nm.

Instruments used during this study included a Hitachi S-900 (in-lens field emission SEM with Gatan cold stage and Gatan DigiScan digital acquisition unit at the Laboratory for Electron Microscopy I, ETH, CH-Zurich) and a Topcon ABT-60 (with a video frame grabber card for direct digitizing of micrographs at the Laboratory for Micro- and Nanotechnologies, Paul Scherrer Institute, CH-Villigen). Only a few of the SEM images are shown here, and thus no further details of the method are provided. The reader is referred to the literature for more information [Bra98], [Eck98], [Nie95].

![Figure 2-2](image)

**Figure 2-2**
Schematic set-up of model glass reactor used for treating catalysts and reactivity investigations. The reactor is made of quartz glass and can handle 15 x 15 mm² samples.

### 2.6 High pressure quartz glass reactor

The treatment of the model catalysts and the catalytic tests were carried out in a quartz glass reactor equipped with standard flow meters (Brooks MFC 5850S) for dosing the gases (Figure 2-2). Using this set-up, samples with a maximum size of 15 x 15 mm² can be examined. Due to size limitations imposed by the UHV equipment and by AFM, sample sizes were usually 10 x 10 mm². The pressure inside
the reactor was measured upstream with a capacity pressure gauge (MKS Baratron 122AA) and maintained at $10^3$ Pa by an electronic back pressure regulator (Brooks PC 5866). The gases used were hydrogen (5.0 quality), oxygen (5.5), and argon (4.8) (SL Gas, Lenzburg). The catalysts were introduced into the reactor through a flange (inner diameter 20 mm) and were positioned on a quartz glass frit. Due to the very rough surface structure of the porous glass frit, the entire model catalyst was exposed to the gas atmosphere. The glass tube was heated in an oven, and the temperature was controlled by a thermocouple in a depression in the glass wall right below the catalyst. The walls of this depression are very thin (less than 1 mm); the inserted thermocouple was placed in the stream of gases, and the measured temperatures were thus assumed to be accurate.

The reactor was connected to a quadrupole mass spectrometer (QMS) by means of a heatable capillary and a pressure reducing valve (Balzers GEV 010) as described in the QMS section. During the measurements (pressure inside the glass reactor: $10^3$ Pa), the GEV 010 was opened just until the resulting leak rate brought up a working pressure in the QMS recipient of $1.0 \times 10^{-4}$ Pa.

2.7 High pressure 4 inch wafer reactor

A stainless steel reactor was built to investigate the catalytic properties of complete 4 inch wafers. The reactor and the glass reactor can both be attached to the equipment that doses the gases. Analysis of the distribution of products and educts was again done by mass spectrometry. For experiments at pressures below $10^2$ Pa, the outlet flange was connected to the UHV recipient with the mounted QMS. For experiments in the pressure range from $10^2$ to $10^5$ Pa, the exhaust gases were pumped away by a rotary vacuum pump. The exhaust line was connected to the QMS by means of a capillary and the GEV 010 as described above.
Figure 2-3 depicts the reactor design and the principle of operation and sealing. The reactor was designed to be a continuous flow reactor, which enables the examination of one or two complete and structured 4 inch wafers. The wafers must be heated uniformly during the experiments. Since the dead spaces inside the reactor volume had to be reduced to a minimum, the reactor was heated through the walls. For this purpose, heating elements were built into the lid and the bottom part of the reactor to provide uniform heating, and the temperature was controlled by three thermocouples.

![Diagram of reactor design and sealing principle](image)

**Figure 2-3**

Reactor design and sealing principle of stainless steel reactor for investigating 4 inch wafers.

Two of the thermocouples connected to an electronic temperature control unit were used to control and minimize temperature differences between the lid and the bottom part. The third thermocouple was located in the middle of the bottom part and controlled the temperature close to the inner surface of the reactor. The reactor walls can be heated to a maximum temperature of 400°C. The temperature above of the wafers was measured once before the reactivity experiments by connecting a thermocouple to the wafer surface through the gas inlet flange. The reactor was heated to 300°C (at a ramp of 4°C/min), and a stream of argon was passed through the loaded reactor (2 ml/min) at a pressure of $10^5$ Pa. It took 20 min from the moment that the reactor walls reached 300°C and the moment when the wafer surface was heated up.
This can be decreased to 10 min when more than one gold wire is used to achieve a better temperature contact between the wafers and the reactor walls. After equilibrium was reached, the temperature remained constant (± 5°C), even if the flow velocity was increased (5 ml/min) or decreased (0.5 ml/min).

Since the inner reactor walls were heated to reaction temperatures, care had to be taken to limit contact between the hot walls and the gas as far as possible. For this purpose and in order to reduce the dead space inside the reactor, the inner geometry was exactly fitted to the wafer requirements, and the inner surfaces of the stainless steel reactor were highly polished. Two wafers with the active sides facing each other were separated by several distance holders of heavily oxidized silicon. The rear sides of the wafers were pressed against two rings of gold wire. The distance holders (ranging in thickness from 0.5 mm to 1 mm) were placed between the surfaces of the wafers so, that the gas stream was evenly distributed over the active surface. This package was mounted to the bottom part of the reactor and the reactor was closed. The gold wires were squeezed between the inner walls of the reactor and the rear sides of the wafers and served as gaskets. Gold was chosen because of its low catalytic activity and high flexibility. The gold wire was of 99.9% quality, had a diameter of 0.25 mm, and was purchased from Johnson Matthey.

The sealing of the reactor functioned well (Figure 2-4). The spectrum shows the mass spectrometer signal for CO₂ (m/z = 44), derived from CO and O₂ at 10⁵ Pa and at a total flow rate of 5 ml/min (CO : O₂ ratio = 2 : 1). The empty reactor (without wafers, distance holders, and gold wires) showed detectable activity in a temperature range from 230°C to 300°C. No carbon dioxide was formed when the reactor was loaded with a package of two oxidized silicon wafers (without palladium on the surface), distance holders, and gold gaskets. The amount of CO₂ in the exhaust gas increased significantly when thin films of palladium (thickness of the films 100 nm) were evaporated onto the wafers. Evaporation masks were used to vary the size of the palladium surface area. Two wafers were produced with 5 and 10 cm² of Pd film on the oxidized surface of the wafer. On the wafer with the smaller amount of Pd, the geometry of the film was orientated according to the direction of the flow of the gas. CO oxidation was achieved with a package of this wafer and a second wafer without Pd on the surface. In a second experiment, a wafer with a Pd area of 10 cm² Pd was
placed in the reactor and combined with a second wafer without Pd. The amount of CO$_2$ formed during oxidation on this second wafer was more than double that of the 5 cm$^2$ film. Therefore, the direction of the flow inside the reactor was influenced by the arrangement of the distance holders so that the entire surface area of the wafers was in contact with the reaction mixture.

![Figure 2-5](image)

**Figure 2-5**

Mass spectrometer signals for CO$_2$ (m/z = 44) emitted by the stainless steel reactor on various model catalysts. Details are given in the text.

However, the design of the steel reactor also revealed considerable disadvantages. First of all, the inner sealing principle requires that the dimensions of all the parts forming the wafer package (wafers, distance holders, gold wires) are exact, with a tolerance of some ten micrometers. Typical dimensions of a 4 inch wafer used in semiconductor industry are shown in Table 2.1

These values are valid for uncovered silicon wafers after polishing. Treating the discs at high temperatures and changing the surface properties (e.g., oxidizing, evaporation of metal films, structuring the surface) may have a negative effect on these parameters. The different layers of the wafers (silicon, silicon oxide, metal films) were heated to temperatures of 400°C. According to [Kuc89], the difference in
the extension coefficients of Si and SiO₂ is about one order of magnitude (3.5 x 10⁻⁶/°C for Si and 0.45 x 10⁻⁶/°C for SiO₂). The length of a silica layer on a 4 inch wafer after heating to 300°C varies by up to 0.02 mm, whereas the length of a silicon wafer varies up to 0.13 mm. Since the value for steel is around 10 x 10⁻⁷/°C, mechanical stress is induced in the wafers during the experiments. This often led to shattering of the wafers so that the reaction mixture and the hot steel walls came into contact.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>125 ± 0.5 mm</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.525 ± 0.02 mm</td>
</tr>
<tr>
<td>Bow and Warp</td>
<td>≤ 50 μm</td>
</tr>
</tbody>
</table>

Tab. 2.1 Part of a specification sheet for a 4 inch wafer used in IC production. Bow and Warp values represent the total deviation of the disk from perfect planarity due to bending (according to [Hop97]).
3. **Basic steps in the manufacture of model catalysts by photolithography**

3.1 *Introduction and general principle of the method*

Photolithography is the process of transferring patterns on a mask to a layer of radiation-sensitive material (called “photoresist” or simply “resist”) covering the surface to be etched, evaporated or treated in different ways. Radiation interacts with the resist in areas where the photons can penetrate the patterned mask. Depending on the kind of resist material, the exposed regions become soluble (“positive resist”) or insoluble (“negative resist”) during the development procedure following the exposure to light. After removing the exposed and developed parts of the resist using a remover solution, the remaining resist material covers the surface as a protective layer against the etching medium. Therefore, the desired pattern is transferred from an initially created mask to the resist and then to the surface.

The wavelength of the radiation, the quality of the photo mask, and the total number of steps in the process are of utmost importance for the size resolution that can be achieved. In modern IC (integrated circuit) production processes, the minimum structure size that can be achieved with optical masks is around 2 μm [Hop98]. Electron-beam lithography, where the pattern is created directly in a very thin photoresist by a scanned focused electron beam without using a mask (direct slice writing, DSW), results in structures smaller than 70 nm but with a significantly lower throughput [Vee98]. The resolution here is mainly limited by so-called proximity effects, caused by the scattering of electrons in the resist layer. Because of the scattered electrons, the resist is exposed not only at the points where the focussed electron beam hits the polymeric layer, but also in the surrounding areas. In research laboratories, features with sizes as low as 1.5 nm were produced by electron-beam lithography [Nak94], [Ill95], [Cum96].

If e-beam lithography is used to create a mask which is used to transfer the patterns to a resist layer on a substrate to be etched, the smallest features that can be pro-
duced are from 100 to 500 nm (in diameter). Therefore, the use of masks not only increases the throughput, but the smallest possible features are also increased by almost one order of magnitude. Laser interference lithography, which will be described in the next section, does not entail the use of photo masks. Hence, the procedure can be seen as a direct slice writing method but with the capability of much higher throughput, since the interference pattern can be increased to cover homogeneously the area of a 4 inch wafer.

3.2 Laser interference lithography

Laser interference lithography was the method of choice for the patterning of oxidized 4 inch Si (100) wafers in this study. The common principles of the method and the experimental set-up will be described here. Y. Bonetti will describe the procedure in more detail in his dissertation [Bon00]. The interference pattern is created by a laser set-up as sketched in Figure 3-1.

Figure 3-1
Schematic set-up of the laser interference exposure system. The beam is split, and the two resulting beams are guided by two mirrors to cause an interference pattern on the wafer surface. With kind permission of Y. Bonetti.
The beam of an HeCd laser (Liconix 4270NB, 70 mW output power at 442 nm wavelength) was split, and the two beams were guided to form the interference pattern on top of the oxidized wafers that were covered with photosensitive material (thinned Shipley S1805 photoresist) by spin-coating. The interference pattern was broadened to homogeneous intensity over the entire wafer surface using lenses and rotating shutter apertures. A single interference exposure results in a pattern of parallel lines of highest light intensity as shown in Figure 3-2.

Figure 3-2

Scheme of superimposed interference patterns on a wafer surface. A single exposure to the pattern leads to parallel lines of highest light intensity on the surface (a). Rotating the wafer by 90° and repeating the exposure (b) leads to the pattern shown in (c), with maximum exposure intensity at the intersections.

Superimposing a second exposure after rotating the wafer by 90° (b) leads to a grid pattern where the photoresist was exposed to the highest light intensity at the intersections of each line of the two interference patterns (c). A single exposure to light usually lasted 5 to 10 min. The length of exposure time was chosen so that the resist layer could be totally removed only at the intersections after developing. During this time, there could be no vibrations in the set-up; therefore, the equipment was mounted in a closed hut on a table which was insulated to eliminate vibrations. After developing and removing the exposed parts of the resist, the wafer was ready for etching or for direct evaporation of the metal films (see Figure 3-3).
3.3 Etching of the substrate and metal deposition

Once the photoresist pattern has been created, the system can be treated in various ways to obtain different model catalyst systems (Figure 3-3). The deposition of metal by evaporation in a vacuum system and the subsequent removal of the photoresist and the overlaying metal ("lift-off") without further pretreatment led to arrays of well ordered metal particles on the flat silicon oxide surface. The diameter of the particles was determined from the diameter of the holes in the photoresist, and the height was controlled by the amount of evaporated metal. Comparable systems were produced by conventional [Kra94] and electron-beam lithography [Jac96], [Jac97], [Yan98], [Joh99], and were tested for catalytic purposes.

Before evaporation, the resist can be used as a protective layer against etching reagents. If the wafer with the patterned resist is exposed to physical or chemical etching, the surface of the silicon oxide is etched only in areas where the photoresist was removed after developing. Therefore, the pattern created in the resist is transferred to the substrate surface. Both physical and chemical etching methods have their advantages and disadvantages. Physical methods such as ion milling enable the etching of various compounds (e.g., in multilayered systems) nearly perpendicular to the surface with high aspect ratios. The etched trenches or pits have almost the same lateral dimensions as the resist pattern, and the depth of the structures is easily controlled by the etching time and the ion flux. However, the resist layer is also sputtered during the etching procedure and a thick resist layer must be used for deep structures. Furthermore, redeposition of sputtered material from the substrate leads to an undefined chemical composition of the substrate surface, especially of the side walls when features with high aspect ratios are required. Our experiments show that long-term exposition of a resist layer to the sputtering ions can lead to a hardening of the resist, which cannot be resolved by the removing solvents after the etching.

Wet chemical etching of silicon oxide with buffered hydrofluoric acid (BE 50-1 from Soprelec SA) was used to produce the pitted samples described in this study. The acid does not affect the resist and is removed completely by subsequent rinsing. Due to the isotropic etching, the resulting structures have larger lateral dimensions than the initial holes in the resist. Etching was done not only perpendicular to the surface (therefore determining the depth of the pits), but also in a lateral direction along
the surface of the SiO₂ beneath the intact resist (known as under-etching, compare Chapter 4.4). The difference in diameter increases with the time that the acid is in contact with the substrate. This did not have a negative effect on our samples. Since the diameter of the resist hole is not affected by the etching procedure, the metal particles produced by evaporation have the same diameters as the openings. This will be discussed in the Results. After evaporating metal films onto the structured substrate, the resist and the overlaying metal was removed.

Figure 3-3
Schematic diagram of the lithographic process for the production of model catalyst systems. Removing the structured resist leads to metal-free substrates (bottom left), whereas evaporation of metal through the resist hollows into the etched pits produces a well-ordered array of metal disks at the bottom of the pits (bottom middle). Skipping the etching step creates ordered arrays of metal dots located on the flat surface (bottom right).
When the resist was removed from the wafer after etching and without evaporating the metal films, a pure, structured silicon oxide substrate was obtained. This system mimics a porous substrate and can be impregnated by methods such as spin-coating of inorganic precursor solutions. Further details can be found in the next section and in the result chapters.

### 3.4 Fundamentals of spin-coating

The principle of spin-coating inorganic precursor solutions for the production of model catalysts on flat substrates was described in the introduction (Chapter 1.3). Spinning is a commonly used technique to prepare coatings of homogeneous thickness on flat substrates [Mey78], [Fla84]. The spin-coating of photoresist material in the microelectronic industry is the best known example. The method was first introduced by Kuipers for the deposition of metal salt solutions. As opposed to porous substrates, a drop of a solution of a metal salt in any solvent will form a single puddle on a flat support. Hydrophobic/hydrophilic surfaces will contribute to this effect in case of aqueous/organic solutions, respectively. On porous supports, the solution will be held back by capillary forces inside the pores, thus leading to a distribution of the metal ions in the pore volume after evaporation of the solvent. The puddle on the flat surface changes its size and shape during the evaporation of the solvent and eventually breaks up into single droplets. When the nucleation concentration of the dissolved salt is reached, crystallization occurs mainly at the borders of the droplets. Therefore, the size and distribution of the resulting particles will differ widely.

Spin-coating leads to a thin film of the precursor solution on the flat substrates (Chapter 1.3). Two processes are involved in the decrease of the thickness of the film: the radial liquid flow, which is a consequence of the centrifugal force, and the evaporation of the solvent. From a mathematical model for spin-coating [Mey78], [Ems58], following equation can be derived:

\[
\frac{dh}{dt} = -2 \frac{\rho \sigma^2}{3 \gamma} h^3 - \Phi.
\]

In this equation \( h \) is the thickness of the film, \( \rho \) and \( \gamma \) are the density and the viscosity of the solution, and \( \omega \) is the rotational velocity. \( \Phi \) is the evaporation rate of the
solvent. Shortly after the substrate begins to rotate, most of the liquid is flung from the wafer. Therefore, the decrease of the liquid film height is mainly due to radial liquid flow in the first few seconds of the spinning, whereas the contribution of evaporation is significant at small film height only. The contribution of radial flow and evaporation become equal for a time $t_1$ and at a thickness $h_1$:

$$2 \frac{\rho \omega^2}{3\gamma} h_1^3 = \Phi.$$  

According to Kuipers [Kui93a], the concentration of the solution remains constant up to this point. From then on, the concentration of the dissolved material will increase until sufficient supersaturation is reached and nucleation starts. Since evaporation of the solvent is the dominant process after the thin liquid film has formed on the surface, the concentration increases evenly over the entire surface of the wafer. Therefore, the points of initial nucleation should also be evenly distributed. The amount of deposited material is determined by the surface area of the wafer and by the thickness of the film. The thickness of the film ($h_1$), however, can be calculated according to

$$h_1 = \frac{\sqrt{\frac{3\gamma \Phi}{2 \rho \omega^2}}}{\omega} ,$$

and the amount of material $m$ deposited on the substrate with a surface area $A$ and $c_0$ as the initial concentration of the solution is given by:

$$m = c_0 h_1 A = c_0 A \frac{3\gamma \Phi}{2 \rho \omega^2}.$$  

Since $\Phi$ is proportional to $\omega^2$ [Mey78], the overall amount of deposited material is, therefore, dependend on the concentration of the solution $c_0$ and on $\omega$ as:

$$m \propto c_0 \omega^{-\frac{1}{2}}.$$  

(An $\omega^{-2/3}$ dependence is expected, if the dependence of the evaporation rate on the rotational velocity would be ignored). It was reported that predictions made after calculating the amount of deposited material, are accurate in a range of 20 %.

Therefore, the amount of deposited material can be controlled. However, it is much more difficult to affect the size and almost impossible to control the arrange-
ment of the metal particles on the surface. Increasing the rotational speed and the concentration of the solution leads to thinner films and more and smaller particles on the surface. This is due to the shorter nucleation times during the fast evaporation of the small amount of solvent from the film. During the short evaporation times, the initially formed nuclei have less time to grow. An opposite effect is observed when the partial pressure of the solvent above the wafer surface is increased. The evaporation rate is decreased and only few but larger particles are found on the surface [Eng97], [Nie99].

To the best of our knowledge, the only attempt so far to influence the arrangement of the deposited clusters on the substrate was carried out by modifying the support with strings of polytetrafluorethylene (PTFE) [Kui93b]. In order to obtain a specific nucleation pattern, a wafer was rubbed with a rod of PTFE prior to deposition of the copper salt solution. The friction produced highly ordered and aligned thin strings of the polymer on the surface. After spin-coating, the copper particles were in straight rows instead of the usual random orientation. It was reported, however, that only poor control of the morphology of the PTFE strings was obtained.

Our approach to improving the regular arrangement of the deposited metal material and to increasing the stability of the resulting systems was to use the well-ordered structures on the pitted substrate surfaces. The use of a flat but structured surface of an oxidized silicon wafer as a base for metal deposition by spin-coating was assumed to lead to model catalysts comparable to the systems reported by Kuipers but with a well ordered arrangement of the metal clusters and a significantly greater stability at elevated temperature. Due to the combination of modified morphology and the specific surface chemistry of the pitted samples, this goal was reached (Chapter 4).
4. Preparation of model catalysts by laser interference nanolithography followed by metal cluster deposition

4.1 Introduction

This chapter describes metal clusters arranged on nanostructured oxidized silicon wafers as model catalyst systems. A photoresist layer spun on top of a wafer was patterned by laser interference exposure. The grid obtained after removing the exposed parts of the resist was used as an etching mask. Pits with diameters of 300 nm and depths between 50 and 60 nm were etched into the oxide layer using wet chemical methods. Two methods were applied to deposit metal clusters (Pd or Cu) in a specific way within the pits. The particles ranged from 10 to 50 nm in height and from 80 to 200 nm in diameter. The model catalyst systems were characterized by atomic force microscopy and X-ray photoelectron spectroscopy. The method presented here enables the production of 4 inch wafers that are covered completely by nanometer-sized structures in a reasonable period of time.

The general principle of preparing and analyzing the model catalysts was described above (Chapter 3). In the section below, some additional details are described for the investigated samples.

4.2 Model catalyst preparation

4.2.1 Nanostructuring of Si (100) wafers

Silicon wafers were oxidized in a semiconductor diffusion furnace in oxygen for 2 h at 1050°C (dry). This resulted in an oxide layer 120 nm thick. Thinned Shipley S1805 photoresist was spun on the wafers to a thickness of about 150 nm. The beam of an HeCd laser was split, and the two beams were guided to form an interference pattern on the wafers. The wafers were exposed for 4 min and rotated at 90° for a further exposition. The resist was developed and was hard baked for 0.5 h in an oven.
at 120°C. The etching of the oxide layer was carried out in buffered HF for 4 min at room temperature. The wafer was rinsed in deionised water and dried in nitrogen.

### 4.2.2 Deposition of metal clusters

The first method used was the evaporation of the metal onto the wafers. Pd was deposited by e-gun evaporation in a Balzers BAK 550 system at an initial pressure below 1*10^{-4} Pa and at a deposition rate of 0.5 nm/sec. Film thickness was controlled by a quartz micro-balance. After deposition, the photoresist and, consequently, the palladium on top of the photoresist was removed ("lift-off") using Shipley Remover 1165 in an ultrasonic bath for 5 min. The samples were annealed in air or under UHV conditions. The oxidized metal clusters (after annealing in air) were reduced using a high-pressure cell. Standard parameters were 1 bar pure hydrogen and a flow of 5 ml/min at 200°C.

The second method included the removal of the photoresist without evaporating of Pd. The structured wafers were cleaned with ethanol and acetone in an ultrasonic bath. Pieces of the wafers (10 x 10 mm^2) were then mounted to a commercial spin-coating equipment held by a vacuum chuck. Wafer fragments were used because of the size requirements of the UHV equipment and the AFM. A wafer piece was rinsed with ethanol and acetone while rotating the sample in order to dry it and to remove dust particles from its surface. Then, about 0.05 ml of a metal salt solution (1.3 wt% Cu(NO_3)_2·3H_2O in 1-butanol as well as 1.2 wt% Pd(CH_3COO)_2 in cyclopentanone) was dropped onto the sample, and rotation was started after 30 sec. The samples were rotated at 2000 rpm at room temperature for about 1 min. The coated samples were heated to 350°C under UHV conditions, while the decomposition products of the inorganic compounds of the precursor materials were monitored by mass spectrometry. Furthermore, some of the samples were treated in a flow-through quartz glass reactor at atmospheric pressure in dry air at flow rates of 10 to 20 ml/min. Reduction of all samples took place in this quartz glass reactor in a hydrogen atmosphere at 10^5 Pa and flow rates of 10 to 20 ml/min.
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4.3 Analysis of model catalysts

X-ray Photoelectron Spectroscopy (XPS) and Temperature-Programmed Desorption (TPD) experiments were performed in the multimethod UHV analysis chamber, described in detail elsewhere [Reb95]. The samples (10 x 10 mm²) can be transferred from a high-pressure cell (10⁻² Pa maximum working pressure) through a preparation cell (standard pressure 1*10⁻⁷ Pa) into the analysis chamber (standard pressure 1*10⁻⁸ Pa) without exposing them to atmosphere. Samples can be cooled to -180°C and heated to 1200°C. XPS measurements were made using non-monochromated Al Kα radiation (1486.6 eV) at 300 W (15 kV, 20 mA).

Atomic force microscope (AFM) images were taken using the Park Scientific Instruments Autoprobe CP equipment in contact (constant force) mode and in ambient atmosphere. The commercially available cantilevers with high aspect ratio tips described in the experimental chapter were used. Scanning Electron Microscopy (SEM) images shown below were taken using the Topcon ABT-60 SEM.

4.4 Results and discussion

4.4.1 Pitted samples with evaporated palladium inside the pits

Figures 4-1 and 4-2 show AFM (a) and SEM (b) images of an etched wafer. Figure 4-1c shows an AFM image of a larger scan area and the perfect arrangement of the pits on the oxidized surface. All measurements reported here were made on the same wafer (except for the image 4-1c), a small region of which was covered by a piece of capton® foil during metal evaporation. Images in Figure 4-1 show the topography of the region that is free of palladium. The depth of the pits is 55 to 60 nm. The silicon oxide was partially etched in one direction, visible as shallow grooves between the pits. This is due to the fact that one of the laser exposures was slightly too long. In contrast to Figure 4-1, the depth of the pits of the sample region loaded with a 20 nm Pd film was measured to be 35 nm Figure 4-2. Therefore, the depth depends on the thickness of the evaporated film as monitored by the quartz micro balance in the evaporation unit.
The shape of the pits as imaged was not influenced by tip geometry, as can be seen in the SEM images of Figures 4-1b and 4-2b. In order to evaporate the metal...
films directly into the pits of an etched sample, evaporation must be done after etching and before removing the structured resist. Figure 4-2c shows an intermittent-contact AFM image of a sample region (that was not covered by capton® foil) after the evaporation of Pd onto the resist material but before the lift-off procedure. The dark hollows in Figure 4-2c are the points where the line patterns of the second interference exposure intersected the lines of the first one. Therefore, at these points, the resist was exposed to the highest light intensity and could be removed completely after developing.

The brightest (and highest) areas between the resist hollows were exposed for the shortest periods of time, whereas the cross-like valleys, stretching from hollow to hollow are due to the parallel interference lines of the two exposures to light. After the lift-off procedure, the individual pits resemble those in Figure 4-2a. The bottoms of the individual pits, formerly smooth and flat (Figure 4-1), were now covered by flat disks of evaporated Pd. The surface of the metal was rather rough with narrow gaps running around the disks. These trenches were caused by the fact that the pits in the silica surface had slightly larger diameters than the resist hollows because of the isotropic etching of the SiO₂ and the shading effects caused by the photoresist during the evaporation of the metal. Etching was done not only perpendicular to the surface (therefore determining the depth of the pits), but also in a lateral direction along the surface of the SiO₂ beneath the intact resist (known as under-etching). However, only the part of the metal passing through the resist hollows reached the bottom of the pits. In the example described, the source of evaporation was far away from the substrate (around 0.5 m), and the direction of the incoming material was nearly perpendicular to the surface. Therefore, the dimensions of the metal disks were a fingerprint of the resist pattern.

Figure 4-3 shows the same Pd-filled sample as depicted in Figure 2-2a but after annealing to 700°C in UHV. The initial heating rate was 1°C/sec. The topographic differences are clearly visible: the metal films became isolated, hemispherical particles with typical dimensions (45 nm in height and around 200 nm in diameter), as shown by the AFM. Assuming that the deposited metal films were shaped like frustums and “reconstructed” during calcination to hemispherical particles, without losing material through vaporization (metal volume constant), these dimensions are
acceptable. Loss of metal due to interdiffusion through the silicon oxide layer into the silicon bulk will be discussed below.

Figure 4-4 shows XPS spectra of the Pd 3d signal. The spectra were recorded for the indicated temperatures on the sample as shown in Figure 4-2 (a and b). The heating rate was 1°C/sec. The measured binding energies are given here, no charge correction was made. The binding energy was 104.5 eV for the Si 2p signal of the SiO₂, which is about 1 eV higher than usually reported for silicon oxide and typical of thick oxide films on insulating samples [Ter96]. Heating to 300°C led to a slight increase in intensity (about 10%) and a slight shift in binding energy from 336.3 (341.4) to 335.9 eV (341.1 eV) of the Pd 3d 5/2 (3d 3/2) signal. Both observations can be explained by the thermo-induced desorption of carbon- and oxygen-containing species from the surface (all samples were exposed to air before being examined in UHV without further cleaning, e.g. sputtering). The first significant changes were found at temperatures around 500°C. A strong decrease in intensity (integral intensity for overall intensity of Pd 3d signal, loss of more than 40% compared to the value measured at 300°C) combined with a further shift in binding energy of 0.3 eV (from 335.9 eV at 300°C to 335.6 eV) occurred after increasing the temperature to 500°C. The intensity continued to decrease even at higher temperatures, as shown in the spectra recorded at 600°C and 700°C. No further shift in binding energies was detected. The decrease in intensity was mainly caused by the changes in the structure of the particles; in the case of the “reconstructed” particles, less of the metal surface area was exhibited, compared to the flat films before annealing.
In the case of the Pd films (as deposited), the intensity of the XPS signal was caused by a surface area of around 0.1 \( \mu \text{m}^2 \) per pit (assuming an average metal film diameter of 360 nm). Once a metal disc changed its shape and has become a hemispherical particle, the total surface area of a single hemisphere is about 60% that
of the original value \((6.2 \times 10^{-2} \mu m^2)\), assuming an average particle diameter of 200 nm. Because the reconstructed particles are spherical caps rather than hemispheres, the exposed area may be even smaller than the latter value. The film thickness (20 nm) and the particle diameters are, in all cases, higher than the escape depth of the X-ray excited electrons. Thus, we assume that the intensity of the XPS signal is directly proportional to the exposed surface of the palladium.

As expected from the above, the Si 2p signal increased, while the intensity of the Pd signal decreased due to the uncovering of SiO₂ inside the pits. Loss of metal due to bulk diffusion (e.g., alloying) or vaporization at the annealing temperatures can be more or less excluded. The calculated volumes of the metal films inside the pits and the hemispheres after annealing are nearly constant using the above mentioned values for thickness and diameters. Thus, no metal was re-evaporated or diffused into the silicon oxide material. If this were not so, then alloying the Pd would have been evident from a shift in binding energy to higher values. This was the case when substrates with very thin oxide layers (only native oxide) at the bottom of the pits were used and will be discussed below. Annealing the catalyst systems in air to 650°C led to comparable results. Because oxygen was present while annealing, the resulting palladium oxide particles were then reduced in pure hydrogen at atmospheric pressure and hydrogen flow rates of 10 ml/min. This treatment did not lead to structural changes in the metal particles trapped inside the pits. Chapter 6 describes extensive treatment of the catalyst systems in oxygen and hydrogen at elevated temperatures and the resulting behavior of the metal particles.

4.4.2 Pitted samples and spin-coating of metal salt solutions

4.4.2.1 Spin-coating of a copper precursor solution

The number and size of the metal particles deposited by spin-coating inorganic salt solutions can be affected by parameters such as the concentration of the solution and the spinning speed [Har95], [Par96]. However, the arrangement of the particles on the surface was affected only slightly by these parameters. Kuipers et al. reported changes in the deposition pattern on a silicon oxide surface after modifying the surface with polymeric material [Kui93b]. We used the nanostructures of the silicon
oxide surface as shown in Figure 4-1 together with the spin-coating procedure to produce model catalyst systems with well-defined deposition patterns. Cu(NO₃)₂·3H₂O, Pd(CH₃COO)₂, and Pd(NO₃)₂ were used as precursor materials. Cu(NO₃)₂·3H₂O was dissolved in n-butanol to give a concentration of 1.3 wt %. The most even distribution of the particles on the structured surfaces was obtained with this solution.

After coating (as described above) the samples, they were investigated by AFM. Figure 4-5 shows a typical topographical view of a sample after coating. Domains such as the one observed on this figure are found all over the surface of the wafer between the flat and visibly clean regions of the structured SiO₂. The covered domains exhibited sharp borders and were found between single pits. The areas contained by such borders were usually hexagons or heptagons (as shown), though rectangles were also found depending on the number of the enclosed pits. Only small amounts of material were located inside the pits. The grainy structures are believed to be particles of copper salt, because such structures were never found on untreated samples; XPS spectra, recorded after the samples were transferred to the UHV system, revealed the copper signal presented in Figure 4-6. Thereafter, the precursor was decomposed by heating from room temperature to 350°C at 1°C/sec in UHV. Figure 4-6 shows the increase in signal intensity and the shift in binding energy of the Cu 2p peaks after calcination. At the same time, the intensity ratio between the Cu 2p signals and the Cu²⁺ satellites (from shake-up transitions) changed significantly.
It is concluded that UHV annealing of the deposited copper nitrate led to the formation of copper metal and copper oxide particles. The binding energy of 933.2 eV for the Cu 2p electrons after the temperature treatment was corrected for charging on the highly insulating samples. The Si 2p peak of the SiO₂ was chosen as a reference for charging during the XPS measurements. The binding energy was 104.5 eV, about 1 eV higher than usually reported for thin SiO₂ layers but typical of thick silica films on insulating samples [Ter96]. Thus, the resulting Cu 2p value for the annealed sample is 932.2 eV, indicating metallic copper species. The remaining shake-up satellites, though with a much lower intensity, indicate that some Cu²⁺ was still present. It was reported that Cu²⁺ is easily reduced under X-ray bombardment to Cu⁰ ([Bro99], and references therein). Because the particles were too large to be reduced completely, some of the copper remained in the Cu³⁺ state. The strong increase in the intensity of the Cu 2p signal was probably due to the shielding of large numbers of copper ions by the uppermost layers of the precursor material on the wafer surface.

![Figure 4-6](image)

**Figure 4-6**

XPS Cu 2p signal before and after UHV annealing at 350°C of a pitted sample, spin-coated with Cu(NO₃)₂·3H₂O in 1-butanol.

The sample was then removed from the UHV chamber and transferred to the AFM. Figures 4-7a and 4-7b show topography and error signal images of the same
scan, 6 x 6 µm² in size (Figure 4-7c is a more detailed view of 4-7b), and Figure 4-7d shows a three-dimensional detail of the sample surface.

Figure 4-7
6 x 6 µm² AFM images showing a) topography and b) error signal of a pitted sample, spin-coated with Cu(NO₃)₂·3H₂O in 1-butanol and annealed in UHV at 350°C. Fig. 4-7c is a detailed view of the sample from Fig. 4-7b and 4-7d a three-dimensional detail from Fig. 7a.

It is obvious that the metal oxide clusters are, for the most part, located inside the pits. The particle in Figure 4-7d is 86 nm in diameter and 11 nm high. Although there are regions on the sample (not shown here) where no particles are observed as well as
other regions where small amounts of what is probably CuO material are located around the pits, most of the material is deposited at the bottom of the etched features. Reduction under mild conditions (atmospheric pressure, 10 ml/min hydrogen flow, temperature below 300°C) led to no observable topographic changes in the shape of the metal particles or in the arrangement compared to the oxide clusters. The changes in topography are due to the high mobility of the Cu precursor species on SiO₂ surfaces [Oet98a]. Anchoring the deposited material appears only during or after annealing the model catalysts.

During the annealing procedure, the particles moved around on the surface until the metal-support interactions were sufficient to anchor the metal particles, for example at steps or kinks on the surface. In the case described here, the “mean free migration path” of the particles was obviously long enough to reach the next pit. The interaction between Cu and SiO₂ is generally believed to be rather weak [Bag92], [Zho93], and, thus, the clusters were expected to be very mobile. Once the particles had fallen into one of the pits, the mobility of the clusters decreased and was limited to the bottom of the pit. If the mobility of the precursor species on the silica was lower than in the copper example due to stronger metal-support interactions, a higher number of metal/metal oxide particles remained on the terraces between the pits after calcination. This will be shown with palladium as metal species.

4.4.2.2 Spin-coating of palladium precursor solutions

The same method of preparation as described above was carried out using 1.2 wt% solutions of Pd(NO₃)₂·2H₂O in 2-pentanone and Pd(CH₃COO)₂ in cyclopentanone. Best results were obtained when a palladium acetate solution in cyclopentanone was used. Figure 4-8a shows one pit filled with worm-like structures of palladium oxide after annealing the sample at 300°C in UHV. Subsequent heating in dry air at 500°C for 1.5 h and reduction at 250°C for 1.5 h in a flow of hydrogen led to terraced plates of the deposited material (Figure 4-8b).

The terraces are about 8 nm high. Although most of the metal was again trapped inside the pits, there was still some material left outside the pits as in the case of Pd. This may be due to the dry air used and the applied temperature which may not have
been high enough to increase the mobility of the particles on the surface. As known from investigations of small metal particles on flat substrates, sintering at elevated temperatures leads to agglomeration of the metal, mainly at steps, kinks, and edges [Che98], [Wit96]. Thus, it was assumed that sintering of particles on the structured samples leads to agglomerations in the pits and at the rims of the pits. However, anchoring of the metal species to the substrate was assumed to occur during calcination and to be dependent on the parameters used in the procedure [Oet98a], [Oet98b]. Model systems with evaporated metal particles on flat oxide supports were usually more susceptible to sintering at elevated temperatures catalysts prepared by wet chemical impregnation. This may be due to the ion exchange mechanism (chemisorption) of the metal salts with the hydrogen ion of the silanol groups on the silica surface. This topic will be treated in more detail below.

![Diagram](image.png)

**Figure 4-8**

Three-dimensional views of AFM images (600 x 600 nm²) of a sample spin-coated with palladium acetate in cyclopentanone after UHV annealing (a) and annealing in air at 500°C and subsequent reduction in H₂ (b).

4.5 Additional remarks

4.5.1 Deposition of palladium colloids on pitted substrates by spin-coating

Metal colloids are nanometer-sized metal particles that consist of several hundreds or thousands of atoms in the metallic state. The particles are usually stabilized against agglomeration by ligands, such as surfactants or polymers. Noble
metal colloids have been investigated thoroughly because of their potential use as catalyst particles. These noble metal colloids, with various metal core diameters and with a narrow size distribution, can be produced quite easily. Functionalized ligand molecules offer a wide range of possibilities for anchoring the colloids to the substrate, for affecting the solubility in various solvents, and for protecting the metal from being poisoned during catalytic reactions. Detailed information on the production of colloids [Bön94], on their properties and potential uses [Sch92] as well as stability of the ligand shell in surface science and catalysis studies [Wit96], [Sha99] can be found in literature. The deposition of a platinum colloid solution onto a flat oxidized silicon wafer by means of spin-coating was reported by [Che98]. After coating (the colloids were dissolved in an ethanol solution to give a concentration of 2.5 g/l), a non-continuous layer was observed on the wafer surface which consisted of entire colloid particles (i.e., metal and ligand material). Reducing the sample in hydrogen led to isolated platinum particles with significantly less shell material on the surface. The particles had diameters of 2 to 3 nm, which is supposed to be the original metal cluster size. However, exposing the systems to oxygen led to the removal of the organic shell from the surface and to significant sintering of the metal particles.

![AFM images](image-url)

**Figure 4-9**

2.2 x 2.2 μm² AFM images of a pitted sample, after spin-coating a solution of PdSB12 colloid (a) and after annealing in air at 350°C (b).

We used a palladium colloid with a metal core diameter of 2.8 nm, stabilized by an organic shell of sulfobetaine [(t-C₁₂H₂₅)(CH₃)₂N(CH₂)₄(SO₃)] molecules, referred
to as SB12, for deposition on the structured substrates by spin-coating. The colloid was produced in the research group of Prof. H. Bönnemann (Max-Planck-Institut für Kohlenforschung, Germany), and kindly given to us by Dipl.-Chem. M. Noeske (Universität Ulm, Germany). The colloids consist of 15 wt% palladium and are highly soluble in water and ethanol. The black powder was dissolved in ethanol (abs.) under inert gas conditions to give a concentration of 1 g/l. The wafer pieces were rinsed with ethanol and acetone and covered with 0.05 ml of the solution. The rotation (2000 rpm) at room temperature took place after 30 sec for 1 to 2 min. Figure 4-9 shows AFM images of two samples after deposition (Figure 4-9a) and after annealing for 4 h at 350°C in air (the samples originated from different wafers with different pit diameters). In contrast to clean wafers, the surface after the coating procedure was rough, while the pits were still visible. It was concluded that a non-continuous layer of colloid material was deposited and that it covered about 30% of the structured wafer surface. XPS spectra (not shown) of these samples indicated the presence of Pd, Si, O, and C, together with small amounts of N and S. Since nitrogen and sulfur were not detected on any other sample, these signal contributions originated from the ligands.

After annealing in pure oxygen, the XPS signals of nitrogen and sulfur were no longer detected, due to the decomposition of the organic compounds [Wit96], [Che98], [Sha99]. The annealed sample showed randomly distributed particles, with a broad size distribution, inside and outside the pits (Figure 4-9b). The particles located on the non-structured areas between the pits had heights of 5 to 20 nm and diameters ranging from 50 to 200 nm. The particles located inside the pits were even larger (having diameters from 100 to 200 nm and heights from 15 to 25 nm). Therefore, the metal...
clusters started to sinter while losing their protective shell under oxidizing conditions. However, the arrangement of the particles before and after sintering was only slightly affected by the structured surface. As can be seen in Figure 4-10, only a small area around one of the pits showed decreased particle density, especially for smaller clusters (the sample was loaded by dipping the wafer into the colloidal solution and showed a significantly higher number of particles on the surface). Therefore, it is concluded that only the small particles of the clean region reached the pit during the annealing procedure. Annealing the samples at 500°C in air led to an increase in the number of larger particles on the surface; there was no significant increase in the number of particles inside the pits. The particles became anchored to the substrate during annealing, when the organic shell was lost and the metal got in contact with the oxide surface. Further annealing led to increased mobility only of the very small particles. These results agree with the results of investigations of comparable colloids deposited on single crystal surfaces of graphite and sapphire [Wit95], [Sch96]. We did not obtain an ordered arrangement of the colloidal particles only in the pits of the pitted surfaces. Spin-coating colloidal solutions of low concentration (0.25 g/l) led to a random distribution of the particles on the surface. Dipping the wafer pieces into the colloid solution (and drying them in air without spin-coating) led to a high catalyst loading (Figure 4-10); however, the particles were distributed statistically after annealing in oxygen. No further attempts were made to achieve a more defined deposition of the colloid particles in the pits.

4.5.2 Surface characteristics of silicon oxides and metal cluster deposition by spin-coating

The silicon oxide layer on top of the silicon (100) wafers formed at temperatures above 1000°C in dry oxygen as described above. Detailed information concerning the growth of SiO₂ on silicon wafers is given by B. Hoppe [Hop98] and S.C. Kao [Kao93]. An amorphous layer of stoichiometric SiO₂ formed under these conditions with hydrophobic siloxane groups (Si-O-St) only. Since the chemisorption of metals/metal salts during wet chemical impregnation takes place via an ion exchange mechanism mainly on the silanol groups (terminal Si-OH groups), the number of
these groups on a given substrate is important for the properties of the substrate. A Si-OH density of \(2/\text{nm}^2\) was proposed for a silicon wafer, oxidized at 500°C in air for 24 hours [Oet98a], but experimental proof was not given. A maximum Si-OH density of about 5 OH-groups/\(\text{nm}^2\) was calculated for amorphous silica, depending on the modification of the silica [Boe66]. Because of the poor wetability by water of oxidized wafer surfaces due to the absence of hydrophilic silanol groups, most of the experiments reported in the literature were conducted with organic solvents (ethanol, butanol). It was reported that even small amounts of water, dissolved as impurity in ethanol, can cause a break-up of the thin layer produced by spin-coating [Doo95], [Oet98a]. The spin-coating of aqueous solutions on hydrophobic oxide surfaces required the addition of surfactants to the liquid phase in order to lower the surface tension of the water. However, this did not give satisfactory results.

Niemantsverdriet and coworkers described a rehydroxylation procedure for silicon oxide layers that had been produced at 750°C. The wafers were treated in boiling water after cleaning them in an \(\text{H}_2\text{O}_2/\text{NH}_4\text{OH}\) mixture; aqueous metal salt solutions were used for spin-coating [Thü97], [San99], [Thii99]. However, the extent of rehydroxylation of the wafers was not determined. The experimental quantification of the number of silanol groups on a given substrate is a demanding task. Detailed investigations of various \(\text{SiO}_2\) modifications were carried out by Boehm [Boe60], [Boe66], Zhuravlev [Zhu87], and Jacobsen [Jaco97]. The results showed a significant loss of silanol groups due to dehydration at temperatures above 450°C. The siloxane groups that formed at this temperature could not be rehydroxylated in a humid atmosphere. Further annealing at temperatures above 800°C removed all the silanol groups and decreased the tensions in the Si-O-Si bindings. This led to inertness of the siloxane groups [Jaco97]. Therefore, the formation of silanol groups by boiling the wafers in water as reported in the literature cannot be taken for granted.

We used anhydrous organic solvents for the deposition of copper and palladium by spin-coating. Therefore, we had no problems with non-wetting behavior or with the high surface tension of water. Due to the high temperature applied during the oxidation of the wafers, we assumed that there would be no silanol groups on the oxide layer. However, wet chemical etching of the surface by hydrofluoric acid induces significant changes. Most of the carbonaceous adlayer, which is usually
present on the surfaces of the wafer after removing the exposed and developed resist (see Chapter 5 for details and cleaning procedures) was removed during the etching procedure. Furthermore, HF dissolves SiO₂ according to:

\[ \text{SiO}_2 (s) + 4\text{HF} (l) \rightarrow \text{SiF}_4 (g) + 2\text{H}_2\text{O} (l). \]

(The formation of the volatile SiF₄ is thought to be the driving force of the reaction [Hol85].) During this process, Si-O-Si bonds were broken and new silanol groups were formed in the presence of an aqueous solution. Therefore, the etched areas on the wafers not only exhibited a significantly different topography compared to the flat plateaus, but were also chemically distinguishable.

Figure 4-11 shows AFM images of two oxidized wafer pieces. Figure 4-11b shows the surface after contact with the HF etching solution, and Figure 4-11a shows the topography without etching. Both pieces were covered with photoresist after oxidation and were put into the HF bath. The photoresist was removed from sample 4-11b before etching; the sample 4-11a was treated with the remover solution after etching. HF contact time was comparable to the pit-etching step on the pitted samples. The surface became increasingly rough during etching. Samples like those shown in Figure 4-11a with a layer of SiO₂ 120 nm thick have root-mean-square roughness values (RMS roughness, based on the standard deviation of the measured values in height) of 2 Å, whereas the value for the etched surface is 4 Å. All the measurements were made with the same tip on single terraces of the wafer without steps or edges and with the utility software of the Autoprobe CP instrument. These values for the oxidized surfaces of our samples (without etching) are lower than 4 Å (± 2 Å), as reported in literature [Suz93], when the surface roughness of thermally grown oxide layers on a silicon (111) wafer was investigated. In those experiments, the oxide layers of the samples were from 10 to 100 nm thick and the oxidation had been performed between 1000 and 1100°C. The RMS value of 4 Å is in agreement with values obtained for oxidized wafers in our laboratory that were not covered with photoresist. Therefore, the initial roughness of the oxide surface may be leveled out due to remaining photoresist material.
Based on these results and considerations, we can explain the preferred deposition of the metal clusters in and around the etched pits (Chapter 4.4.2). During the lithographic process, the HF solution etches the hydrophobic surface of SiO$_2$ in the pit areas. Therefore, at these points, the silicon oxide layer is modified in terms of topography (pit formation, roughening of the surface) and chemical composition (removal of carbonaceous adlayers, rehydroxylation). The modifications make the pits preferred adsorption and nucleation sites during spin-coating and calcination of the model catalyst systems. Since the etching of the amorphous silica material appears isotropic, the silica layer is etched both perpendicular and lateral to the surface, beneath the intact resist. This is known as under-etching. In certain cases, this can lead to etched areas between the pits. AFM images of samples in Chapter 4.4.1 show that shallow grooves between the pits are visible. Because one of the two exposure times to the laser interference pattern was slightly too long, the remaining resist in this direction was weakened significantly. The HF solution can penetrate the interface between the silica and the resist due to capillary forces at points, where the resist is more flexible. We propose that small amounts of the etching solution reach and modify the silica surface surrounding the pits on most parts of the wafer. Even if this is not always visible on AFM images, it is traced by the patterned deposition of the copper nitrate particles (Chapter 4.4.2). The interactions between the metal salt and the modified substrate surface are obviously strong enough to lead to nucleation at these sites, whereas in the case of weak metal-support interactions (as is the case in
the Cu/SiO₂ system) the bonds are broken during annealing of the samples. The metal particles are located mainly inside the pits after annealing or calcination. For systems known for stronger metal-support interaction (Pd/SiO₂), sintering during annealing is less significant (if the metal was deposited by wet chemical routines).

4.6 Conclusions

Two methods were studied for the controlled deposition of metallic particles onto a nanostructured silicon oxide surface. The evaporation of palladium through a patterned resist into pre-etched pits as well as the wet chemical impregnation method led to perfectly ordered arrays of metal clusters with predictable sizes. The size of the clusters does not yet reach the lower nanometer region, as is possible by means of electron beam lithography. However, compared to most model systems known thus far, these arrays have great potential because of the unique combination of uniformity, stability and large metal surface area (they can be produced with a large overall area on 4 inch wafers). Therefore, the catalysts provide sufficient metal surface area for reaction studies, even at atmospheric pressure. Optimizing the preparation parameters (especially reducing the thickness of the evaporated films) will help to decrease the size of the clusters.
5. The properties and behavior of nanostructured model catalysts exposed to catalytic conditions

5.1 Introduction

This chapter deals with the production and properties of a series of nanostructured model catalysts on 4 inch Si wafers as supports. As shown in the foregoing chapter, a single wafer has $10^9$ to $10^{10}$ pits on an otherwise flat silicon oxide surface after wet chemical etching. The preparation and analysis of these model catalysts are described in the experimental section and in the previous chapter. The etched pits of the wafers of the samples described here have diameters of 200 to 400 nm and depths between 50 and 70 nm. They were loaded with metal particles by evaporation of palladium and, in a second series, with silver. The evaporation of silver was done in the same evaporation unit (Balzers BAK 550) and with the same parameters as used for the palladium deposition. The resulting model catalysts are remarkably stable against sintering.

Sintering of catalytically active metal particles at elevated temperatures and in reactive gas atmospheres is a well known process that deactivates a catalyst through the loss of metal surface area and the loss of the specific properties of small particles [Ste87], [Pet87]. To prevent particles from sintering, high surface area supports are used in actual catalysis and the preparation steps are chosen in such a way that the particles become anchored to the support during the procedure. In model catalysis research, metal particles are usually deposited onto flat substrates. Since the substrates are flat on an atomic level (average roughness on thermally grown oxide films is in the range of Ångstroms), they have only few steps, edges, or kinks, the preferred anchoring places for metal clusters after deposition. Therefore, sintering is a major problem of known model catalysts when exposed to elevated temperatures and oxidizing gas atmosphere, especially when the metal clusters are produced by evaporation techniques [Oet98b]. In summary, the stability of a catalyst under given conditions depends strongly on the substrate (material, surface structure, and chemical
pretreatment) as well as on the method of preparation and deposition of the metal particles.

It will be shown here that structuring the surface of the oxidized silicon wafers leads to model catalyst systems that are stable even under harsh catalytic reaction conditions. The results obtained show that this is especially true for systems where the active metal particles are deposited by evaporation. In comparison, samples of nanostructured palladium particles were produced by lithography but without etching the pits into the flat surface. Metal particles were thus positioned on a flat SiO$_2$ surface after lift-off, comparable to systems reported in [Kra94] and [Yan98]. The topography and chemical composition as well as the changes induced by the reaction conditions, including stability and chemical behavior of the nanostructured systems, were investigated. Furthermore, special attention was given to the carbon contamination of the surface of model catalyst systems produced by lithography. Typical surface science cleaning techniques were compared to cleaning steps used in actual catalysis. To determine the usefulness of the systems in catalysis, a specially designed high-pressure quartz glass reactor (see the experimental chapter) was developed for cleaning and for catalytic investigations.

5.2 Results and discussion

5.2.1 Deposition of metal particles on pitted and flat surfaces

5.2.1.1 Behavior of palladium particles under UHV conditions

The behavior of palladium particles deposited in the pits of a structured silicon oxide surface at elevated temperatures was described above. In UHV, annealing at temperatures up to 500°C did not lead to significant changes in the topography of the samples. Neither the shape of the Pd films, nor the arrangement on the substrate surface was affected by temperature. Minor changes in the chemical composition of the model catalyst, as observed by XPS spectroscopy, were assigned to thermo-induced desorption of carbon- and oxygen-containing contaminations from the surface. After exposing the sample to temperatures above 500°C in UHV, a strong decrease in the intensity of the Pd 3d signal and, at the same time, a slight shift in the
binding energy to lower values were observed (Figure 4-4). These changes were accompanied by significant changes in the structure of the particles. The formerly flat, disk-like films reshaped to form hemispherical particles, but no sintering was observed. The conclusion was drawn that no material was lost as a result of evaporation or of losses through the diffusion of material into the bulk, because calculating the volumes of the disks before and those of the hemispheres after annealing resulted in constant values for both shapes. Therefore, reshaping the particles led to the decrease in the intensity of the XPS signal, because the hemispherical particles exhibited 40% less surface area than the initial disks after the annealing procedure. However, effects like bulk diffusion into the silicon of the palladium have to be considered when using very thin silicon oxide layers between the silicon and the metal. This will be discussed in more detail in the last section of this chapter.

The regular arrangement of the metal particles on the pitted samples even after annealing is supposed to be a direct consequence of the pre-structured surface. For the preparation of the pitted samples, the silicon oxide surface was etched with hydrofluoric acid before the evaporation of the metal. In order to evaporate the metal films simply onto the flat surface, evaporation is done after structuring and before removing the resist pattern. Figure 5-1 shows an AFM image of a typical sample after evaporation of Pd and after the lift-off process. The metal films (thickness of the films on this sample: 7 nm) are positioned on a flat silicon oxide layer (120 nm thick), the average diameter of the Pd discs is 290 nm.
One of these samples (Pd film thickness: 20 nm) was exposed to 700°C in UHV for 5 min. Figure 5-2 shows two scanning electron microscope images of this sample. It is obvious that, even after the short annealing time in the absence of oxygen or water (in the gas phase), a large amount of the Pd clusters started to move around on the surface, whereas others remained correctly arranged. The individual particles show the same reshaping behavior as observed on the pitted samples but tend to sinter and to form large metal cluster agglomerates. This was never observed on pitted samples under the same conditions.

Figure 5-2
SEM images of lithographically produced Pd particles (initial height of the deposited particles: 20 nm) on a flat SiO₂ surface. The sample was annealed in UHV to 700°C for 5 min.

As already discussed in Chapter 4, etching the silicon oxide layer by hydrofluoric acid leads to significant changes not only in topography (pit formation), but also in the chemical composition of the surface. Since during the pit etching a considerable amount of SiO₂ (around 60 nm in depth) is removed in the regions of the exposed resist, eventually remaining resist layers at these points are removed together with the dissolved silica, before the metal films are deposited by evaporation. Thus, the metal films at the bottom of the pits have a metal/silica interface, hardly influenced by contaminations of any kind. The situation is different, if the etching step is skipped.
Then, the metal is evaporated onto regions of the wafer that were in contact with the resist layer. Therefore, all polymeric material of the resist that has withstood the remover solvent, is located between the silica and the metal. Thus, the metal-support interactions are reduced strongly. This leads to the mobility of entire metal particles with diameters of nearly 300 nm over micrometer distances. The phenomenon was shown for metal crystallites supported by carbon that sintered mainly due to migration of the entire crystallite, especially in H\textsubscript{2} and O\textsubscript{2} atmospheres [Bar93]. The behavior was explained by metal induced reactions of the carbonaceous material to CH\textsubscript{4}, CO or CO\textsubscript{2}. The gases are thought to lift the metal particles, causing them to float over the surface. Evidence for this mechanism are TEM images, showing channels left behind by the migrating particles. Similar behavior was reported for Ni crystallites, supported by a carbon-contaminated alumina model support [Ruc84]. For clean alumina model substrates a completely different behavior was reported. Therefore, impurities play an important role in the sintering behavior of supported metal clusters, especially on flat model supports.

5.2.1.2 Behavior of palladium particles under oxidizing and reducing conditions

In contrast to the UHV results obtained on the dot samples, the regular arrangement of the metal clusters inside the pits was retained, even when the pitted catalysts were exposed to an oxygen-containing atmosphere at elevated temperatures. To prove this, a sample with a Pd film (thickness of 20 nm) was treated in a quartz glass reactor in a flow of oxygen and hydrogen at temperatures up to 400°C. The first oxidation/reduction cycle was performed at 200°C at an overall pressure of about 10\textsuperscript{5} Pa. First, the sample was exposed to an argon/oxygen mixture for 60 min, then the reactor was purged with pure argon at the same temperature and the flow of the argon/hydrogen mixture was started. The gas flow was 2 ml/min, and the argon/oxygen and argon/hydrogen ratios were 1:1. This cycle was repeated three times. The temperature of the oxidation treatment was then increased to 350°C and kept at that temperature for 10 hours (argon/oxygen flow). Finally, the temperature was increased and remained constant at 400°C for 60 min. The system was then cooled down to 200°C, and the gas flow was switched to the argon/hydrogen mixture for two more hours. The sample was immediately transferred to the UHV system for
XPS measurements. The results are discussed below. The topography was investigated by AFM after the XPS measurements. Although the temperature of the reactor did not exceed 400°C (measured on the outside walls of the glass reactor tube), the particles in the pits are reconstructed in a way similar to that described after the UHV annealing at 700°C. Comparable oxygen-induced variations in the shape of the late transition metals on oxide surfaces were reported for Pt on CeO₂ in oxidizing atmospheres at atmospheric pressure and temperatures around 700°C (Johannson et al. [Joh99]). The Pt particles in that study were produced by means of e-beam lithography and reconstructed from polycrystalline disks to 3D single crystals, as shown by SEM measurements. In our study, it was not possible to determine the crystallinity of the Pd particles inside the pits by AFM because of the tip-induced change in the shape of the particles (the corners became curved). However, according to the smooth metal surfaces and the extremely steep slopes of the side walls of the particles, 3D crystallinity is likely. Furthermore, during the oxidation/reduction cycles the condensation of water was observed inside the glass reactor on the colder parts of the equipment outside the oven. Therefore, it is concluded that the catalyst was active for hydrogen oxidation. Since the reaction is strongly exothermic, the temperature at the surface of the Pd particles can easily exceed 400°C during the reaction. Nevertheless, sintering was never observed.

5.2.1.3 Behavior of silver particles under oxidizing and reducing conditions

Also for systems that are more susceptible to sintering at elevated temperatures, no sintering was observed. To prove this, pitted samples with silver instead of palladium films inside the pits (15 nm film thickness), were exposed to oxygen at elevated temperatures. Figure 5-3 presents the topography of such a silver sample before (left) and after (right) the treatment in flowing oxygen. The sample was placed in an oxygen flow (1 ml/min) at 400°C for 30 min. While it has been reported that arrays of lithographically produced silver clusters on flat silica surfaces were erased under these conditions [Yan98], this did not happen with our samples. The metal films inside the pits again reconstructed to isolated particles, but the reshaped particles did not leave their pre-determined location.
5.2.2 Cleaning the model catalysts

After the lift-off procedure, X-ray photoelectron spectra of pitted samples indicated a large number of carbonaceous species on the surface. This contamination is probably due to an overlayer of polymeric material. The palladium samples were not able to chemisorb and desorb carbon monoxide. Therefore, it was concluded that the Pd particles were covered by carbon adlayers [Jac97]. Figure 5-4 shows the C 1s spectra measured on the samples shown in Figure 4-2a in the foregoing chapter. Spectrum a) shows the C 1s signal before treatment and after several cleaning steps (b-g). Spectra b) and c) were recorded for the same sample as spectrum a). Spectra d) – f) were measured on a second sample and spectrum g) on a third sample, each with an initial amount of carbon contamination comparable to that given for a). The catalyst of spectrum a) was treated for 30 min in a 1:1 mixture of H$_2$SO$_4$ (conc.) and H$_2$O$_2$ (30%) and rinsed with bidistilled water and ethanol (absolute, puriss.) prior to recording spectrum b). Without transferring the sample to the atmosphere, it was Ar$^+$ sputtered for 30 min at 4 keV ion energy (graph c). The relative intensities given in Table 5.1 are based on the integration of the individual peak areas after subtracting the background and satellites. The resulting values were divided by the relevant
atomic sensitivity factors and were normalized to the intensity of the Si 2p peak. It is clear that some but not all of the carbon on the surface can be removed under the conditions applied.

Figure 5-4
XPS spectra of the C 1s signal of the pitted samples evaporated with 20 nm Pd. Spectra are recorded at room temperature after cleaning (Table 5.1). All spectra are recorded at a pass energy of 50 eV.
Cleaning and activation of real metal catalysts are usually carried out through oxidation/reduction cycles. Thus, a sample was treated in a quartz glass reactor as described above. After three cycles at 200°C and 10^5 Pa (2 hours in a flow of argon/oxygen, 2 hours in a flow of hydrogen/argon), followed by 10 hours at 350°C and 1 hour at 400°C in argon/oxygen, the sample was reduced for two more hours at 200°C in a hydrogen/argon atmosphere. During transfer to the UHV system, the sample was exposed to atmosphere for 5 min. In order to remove any adsorbed species from the surface, the sample was flashed to 400°C in UHV for 5 min.

Table 5.1
XPS intensities of the C 1s and Pd 3d peaks relative to the Si 2p signal. Spectra a) - c) are recorded on the same sample, spectra d) – g) on a second sample and spectrum f) on a third sample. All samples are pieces of the same 4 inch wafer.

<table>
<thead>
<tr>
<th>Graph</th>
<th>Sample pretreatment</th>
<th>C 1s</th>
<th>Pd 3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>as produced, after lift-off</td>
<td>0.37</td>
<td>0.17</td>
</tr>
<tr>
<td>b)</td>
<td>30 min in H2O2/H2SO4 at room temperature</td>
<td>0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>c)</td>
<td>Ar+ sputtering at 1.10^-4 mbar Ar, 4 keV, 30 min</td>
<td>0.07</td>
<td>0.17</td>
</tr>
<tr>
<td>d)</td>
<td>30 min oxidation at 1.10^-6 mbar O2 at 300°C 30 min reduction at 1.10^-6 mbar H2 at 200°C</td>
<td>0.11</td>
<td>0.2</td>
</tr>
<tr>
<td>e)</td>
<td>Ar+ sputtering at 1.10^-4 mbar Ar, 4 keV, 30 min 30 min oxidation at 1.10^-4 mbar O2 at 300°C 30 min reduction at 1.10^-4 mbar H2 at 200°C</td>
<td>0.05</td>
<td>0.2</td>
</tr>
<tr>
<td>f)</td>
<td>repetition of procedure described in e)</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>g)</td>
<td>repeated high-pressure oxidation/reduction cycles as described in text</td>
<td>0.05</td>
<td>0.07</td>
</tr>
</tbody>
</table>

As described above, the disk-like films inside the pits reshaped under the oxidizing conditions of the cleaning cycles to give three-dimensional particles with a high aspect ratio. Therefore, the intensity of the Pd 3d peak decreased strongly (comparable to the decrease in intensity after UHV annealing at temperatures above
500°C). However, the amount of carbon on the surface (Figure 5-4, graph g) was comparable to that after repeated sputtering and high-vacuum oxidation/reduction cycles (graph e and f). Repeating the high-pressure treatment in oxygen at temperatures up to 600°C did not lead to a further decrease in the intensity of the C 1s signal. During the oxidation/reduction cycles, water condensed on the colder parts of the glass tube of the reactor after the gas flow was switched from oxygen to hydrogen and vice versa. Because purging with pure argon after each oxidation (reduction) was done only to an ensure that about half of the oxygen (hydrogen) was pumped out of the reactor before the hydrogen (oxygen) flow was restarted, water probably formed on the Pd particles. Water condensation was not observed in the absence of Pd-covered systems. Therefore, the surface of the model catalysts can be cleaned by means of the same methods used for preparing actual metal catalysts. As will be shown in the following chapter, the samples were active for carbon monoxide oxidation after the treatments described here. Since the surface science cleaning methods did not produce particularly good results and because homogeneous sputtering of the entire surface area of a 4 inch wafer requires large and expensive facilities, cleaning as well as activation through oxidation/reduction cycles in a simple glass reactor are suitable alternatives. This, however, requires that the systems are sufficiently stable under the conditions applied.

5.3 Additional remarks

5.3.1 Palladium silicide and SiO formation on samples with thin silicon oxide layers

The restructuring of the metal films to 3D particles with a significant lower surface-to-volume ratio was described above. It was concluded that this is responsible for the loss of XPS signal intensity after the high temperature treatment. However, two other explanations must also be considered. The first is the migration of the palladium into the silicon bulk and, therefore, the formation of palladium silicide [Sco83]. This diffusion process is a widely used method to enrich surface regions of semi-conductive silicon by pre-deposited dopants, and is intensively investigated for
Chapter 5

the near-noble metals nickel, palladium and platinum [May92]. Due to the concentration gradient, the doping material (here: palladium) migrates into the silicon and, on the other hand, the silicon moves into the metal dots. These processes result in a loss of active Pd surface. The second possible effect is the formation of volatile SiO at the Si/SiO\(_2\) interface under high temperature due to the decomposition of SiO\(_2\) (under UHV conditions) or partial Si oxidation (in the presence of oxygen) [Tro85], [Kob92], [Sun92]. Redeposition of the volatile species in form of Si or SiO\(_2\) on the Pd particles can form a shielding layer, therefore causing a poisoning of the metal surfaces and the decrease in the intensity of the XPS signal. Since the decomposition of SiO\(_2\) requires temperatures above 800\(^\circ\)C (900 – 1000\(^\circ\)C), and SiO in the presence of oxygen desorbs from the surface only at temperatures above 700\(^\circ\)C, neither process can explain the effects observed in our studies. Therefore, only the migration of palladium into the silicon bulk must be considered as a possible pathway for the loss of metal surface.

5.3.2 The influence of thick silicon oxide layers

However, migration can be prevented by preparing thick oxide layers between the metal and the semiconductor. The remaining oxide layer at the bottom of the pits of all the samples discussed in this thesis was at least 60 nm thick. Usually, 10 nm oxide layer are considered to be sufficient for an effective diffusion barrier. Here we present results for the UHV annealing of a nanostructured Pd/SiO\(_2\)/Si system with a very thin silica layer between the metal and the semiconductor. The results differ significantly from the results obtained on the samples described so far. The experiments were performed on a sample from which the oxide layer at the bottom of the pits had been removed, thus leading to an interface consisting only of native silicon oxide. Figure 5-5 (left side) shows XPS spectra of the Pd 3d signals recorded on such samples as compared to the spectra of the sample with the thick oxide layer (right side), as shown before in Figure 4-4 in the foregoing chapter, after annealing at the same temperatures. The signal again showed a 40% decrease in the intensity of the Pd 3d signal of the initial values. However, in this case a shift in binding energy of 1.4 eV to a higher binding energy was observed between the spectrum recorded at room temperature and after annealing the catalyst at 700\(^\circ\)C. The formed palladium species
could not be reduced in hydrogen to the metal state \((\text{Pd}^0)\). Furthermore, the topography of these samples (Figure 5-6 before (left) and after (right) the annealing) differed from that of the catalysts with the thick oxide interface (Figure 4-3 in the previous chapter). Only flat, very broad particles were detected at the bottom of the pits, thus indicating diffusion of the palladium towards the silicon bulk.

![Figure 5-5](image)

**Figure 5-5**

Comparison of the XPS spectra of the Pd 3d signal of the pitted samples with only native (left side) and thick silicon oxide layer (60 nm, right side) between the silicon and the palladium.

These results lead to the conclusion that the deposited metal diffused into the silicon and formed silicides. The observed binding energies and shifts after annealing coincided with values reported for the formation of PdSi, Pd2Si, and Pd3Si from the palladium metal and the silicon semiconductor [Cro83], [Gru82].
In contrast, the volume of the metal films and particles was constant on all samples with thick oxide layers. There were no shifts in binding energy to higher values at temperatures up to 700°C except for samples under oxidizing conditions, on which the formed palladium oxide was completely reduced in hydrogen. Therefore, restructuring of the metal films to 3D particles is probably the only reason for the loss of XPS signal intensity.

![AFM images](image)

**Figure 5-6**
AFM images (three-dimensional views, 0.6 x 0.6 μm²) of a sample with only a native oxide layer between Pd and Si before (a) and after (b) annealing the sample at 700°C in UHV.

5.4 **Conclusions**

Palladium and silver particles were deposited onto a nanostructured silicon oxide surface. For comparison, identical clusters were created on a flat substrate surface. The stability of the arrays produced on the nanostructured sample was significantly higher, even under harsh catalytic conditions. The perfectly ordered arrays of metal clusters showed significant amounts of carbon-containing contaminants on the surface, which is common in systems produced by lithography. Typical surface science methods of cleaning the surfaces did not give satisfying results. However, since the pitted model catalysts showed that the well-ordered arrays were uniquely
stable, high temperature treatments under oxidizing conditions did not disturb the arrangement of the metal particles. This seems to be a promising method for activating the metal clusters for catalysis and will be discussed in the next chapter. Furthermore, the necessity of using thick silicon oxide layers on top of the silicon wafers so as to avoid the formation of silicide at elevated temperatures was shown.
6. Foils, films, and nanostructured surfaces: A comparative study of model catalyst surfaces

6.1 Introduction

A polycrystalline palladium foil and palladium films of various thickness, supported on oxidized silicon wafers, were treated under catalytic conditions in a gas flow reactor. Their topography and chemical composition were investigated before and after exposure to oxygen and hydrogen by atomic force microscopy and X-ray photoelectron spectroscopy. The results were compared with those of nanostructured palladium model catalysts measured under the same conditions. The nanostructured samples were prepared on oxidized silicon wafers by laser interference lithography and subsequent metal evaporation. Hydrogen and carbon monoxide oxidation were used as test reactions in a quartz reactor at $10^5$ Pa pressure and at temperatures up to 600°C. All palladium-containing systems were catalytically active after several activation cycles. Nanostructured silver model catalysts were treated in the same way for comparison.

The high temperature treatment at atmospheric pressures in oxygen and hydrogen proved to be highly effective in decontaminating the surface of the catalysts and especially in ridding it of carbon-containing species. Significant changes in the topography of the metal surfaces due to catalytic etching were observed after treatments at 400°C and 600°C in the presence of oxygen and hydrogen. While larger palladium clusters on the flat SiO$_2$ surface tended to sinter and to form larger aggregates, the silver particles started to split and spread over the substrate.

The aim of this investigation is to compare the chemical and topographical behavior of a pure bulk sample (foil) and a number of model catalysts under the same catalytic conditions when the elongation of the metal layer is restricted in one (films) or more (particles) directions. The probability that a single atom, initially located in the bulk of a very small metal cluster, migrates to the surface due to restructuring processes during a catalytic reaction is significantly higher than for a single atom in a
larger particle. This may play an important role in the catalytic performance of multi-component particles such as alloys, where the ratio of the various species on the surface is essential for the properties of the system. Phenomena such as sintering, redispersion, and changes in the particle shape of catalysts, induced by processes such as thermal and catalytic etching [Wei96], have been investigated in the past in detail using important catalytic metals (e.g., silver, copper, platinum, and rhodium). In semiconductor research, emphasis has been placed on elements such as silicon, aluminum, and titanium [Bec93]. There has been little, if any, cross-referencing between the two research fields. To the best of our knowledge, little has been published on palladium-based systems.

It is usually difficult to compare results obtained with model systems in catalysis and surface science, because the results are influenced by the methods of preparation, the quality and the purity of the materials used, as well as by the technical equipment. Carbon and other contaminants strongly influence the equilibrium shape of supported metal particles, as known from Pt catalysts [Wei96]. Therefore, with the exception of the foil sample, all the model catalysts studied in this chapter were prepared as far as possible on identically prepared substrates with the same parameters.

6.2 Preparation of the model catalysts and instrumentation

A polycrystalline palladium foil (Johnson Matthey, 99.9 % metal based purity, thickness 0.25 mm) was used as a reference for all the other palladium samples. The foil was cut into pieces of approximately 10 x 10 mm², and the pieces were cleaned in ethanol and acetone in an ultrasonic bath prior to use. The film samples and the nanostructured model catalysts were prepared on heavily oxidized silicon (100) wafers. The 120 nm thick oxide layer on the wafers was produced by annealing the wafers in dry oxygen. Depositing of Pd and Ag films was done by electron-gun evaporation of the metal on the oxidized wafers in the Balzers BAK550 system at an initial pressure below 10⁻⁴ Pa. The films were deposited at rates of 0.3 nm/sec (10 nm films) and around 10 nm/sec (500 nm films). The wafers were kept at room temperature during evaporation, and the thickness of the evaporated films was controlled by a quartz
microbalance. The preparation of the nanostructured model catalysts was performed according to the procedures described in the foregoing chapters.

The treatment of the model catalysts and the catalytic tests were carried out in the quartz glass reactor as described in the experimental chapter. The X-ray photoelectron spectroscopy (XPS) experiments were carried out with a constant pass energy of 50 eV for all spectra. All spectra reported below are raw data.

All the samples were transferred from the glass reactor to the UHV equipment and back again in air. The samples were fixed on the sample rod by the frame-like construction shown in the experimental chapter and the time of exposure to air was kept as short as possible (around 2 min). In the preparation chamber of the UHV system, the catalysts were flashed to a maximum temperature of 400°C (after exposure to 400°C or 600°C in the glass reactor; fresh samples were not flashed prior to UHV investigations) in order to remove any adsorbed material from the surface of the samples before transferring them to the analysis chamber.

After the XPS analysis, the topography of the model catalysts was imaged by atomic force microscopy. The AFM was used in ambient atmosphere in contact (constant force), intermittent, and non-contact mode, depending on the stability of the metal films or particles on the samples.

For all experiments described below, wafers fragments (10 x 10 mm²) were used because of the size requirements of the UHV equipment, the AFM, and the reactor.

6.3 Results and discussion

6.3.1 Characterization of the untreated catalysts after preparation.

6.3.1.1 XPS analysis of the fresh catalysts

Figure 6-1 shows XPS spectra of the Pd 3d signal. The spectra of the various model catalysts were recorded as they were received (foil) or produced (all other samples). Dust particles were removed from the surface of the samples by rinsing them with a few drops of acetone and ethanol before the measurements. The upper three spectra were recorded on the Pd foil and the two film samples. The binding energy for the Pd foil was 334.8 eV and 340.1 eV for the Pd 3d₅/₂ and the Pd 3d₃/₂
peaks, respectively. The same values (± 0.1 eV) were obtained for the film samples. Therefore, the binding energy values for all three samples were in agreement with literature values [Bri90] for palladium in the metallic state. No charging was observed. Thus, it is presumed that the Pd on both film samples was deposited as closed layers on top of the SiO$_2$ on the silicon wafer. This was confirmed by the absence of the Si 2p peak in the XPS spectra of the 500 nm thick film. Only a very weak signal contribution from SiO$_2$ was observed on the 10 nm film sample, probably due to minor scratches in the film.

Since the amount of palladium on the nanostructured catalysts was much smaller than on the film samples, the Pd 3d signals were less intense. For the sake of clarity, these three signals were enlarged in Figure 6-1 (note the difference in the lower and upper scale of the graph). In the case of the nano-pits, the substrate was etched before evaporation, whereas in the case of the nano-dots the particles were located on the flat oxide surface. Seven and 20 nm of palladium were evaporated through the structured photoresist on the dot samples. Specific differences in the behavior of the two dot samples in the various treatments will be discussed later. The etched sample was loaded with 20 nm of palladium, and the pits were 60 nm deep before the evaporation.

The intensity of the signal of the 20 nm (7 nm) dot sample was only 12% (8%) of that of the average intensity of a film sample, whereas the intensity of the pitted samples (Pd film in the pits was 20 nm thick) reached only 9%. These values were in good agreement with AFM measurements, where a Pd coverage of 14% was calculated for the 20 nm dot samples and of 12% for the pitted samples. The XPS results indicated a lower coverage in both cases, the difference between the values obtained by XPS and AFM being larger for the pitted sample. We propose two explanations. First, there was a significant amount of carbon on the surface of both types of samples (Table 6.1). In the case of the pitted samples, the carbon-to-palladium signal intensity ratio was nearly double that of the dot samples. Since the number of carbon-containing species on the silicon oxide should be comparable in both cases, it was assumed that most of the carbon was located on or around the palladium particles. Second, the Pd signal on the pitted sample was shielded to a great extent by the carbon layer. Furthermore, the slightly sloping walls of the Pd particles on the pitted samples were very close to the SiO$_2$ rims of the pits. It was expected that
there is a small, if any, signal contribution from the side-walls of the particles, in contrast to the dots, which were exposed on the flat surface.

Figure 6-1
XPS spectra of the Pd 3d signal of the model catalyst samples as received/produced:
- a) foil;
- b) 500 nm film;
- c) 10 nm film;
- d) 7 nm dots;
- e) 20 nm pits;
- f) 20 nm dots.
The binding energies of both samples were identical (335.8 eV and 335.9 eV for the Pd 3d$_{5/2}$ peaks, 341.1 eV and 341.2 eV for the Pd 3d$_{3/2}$ peaks, respectively). These values were about 1 eV higher than the values for the foil and the film samples. Since the samples were prepared and treated in the same way as the film samples, this difference was not due to changes in the chemical oxidation state but to the isolated position of the clusters on the insulating support material. The binding energies of the Pd 3d signals (336.0 and 341.3 eV) were the same as on the thin Pd film (thickness of the Pd layer 10 nm), after the sample was annealed to give isolated particles (compare Figures 6-3c and 6-4c. The binding energy of the Si 2p peak of the SiO$_2$ was between 104.1 and 104.3 eV, which is also about 1 eV higher than usually reported for silicon oxide and typical of thick insulating films [Ter96].

Table 6.1
XPS intensity of the C 1s peaks relative to the Pd 3d signal on the various model catalysts. Details of treatments are given in the text.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s intensity relative to the Pd 3d signal after various pre-treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
</tr>
<tr>
<td>Pd foil</td>
<td>0.42</td>
</tr>
<tr>
<td>Pd film 500 nm</td>
<td>0.22</td>
</tr>
<tr>
<td>Pd film 10 nm</td>
<td>0.22</td>
</tr>
<tr>
<td>Pd dots 20 nm</td>
<td>0.19</td>
</tr>
<tr>
<td>(7 nm)</td>
<td>(0.22)</td>
</tr>
<tr>
<td>Pd (pits) 20 nm</td>
<td>0.38</td>
</tr>
</tbody>
</table>
6.3.1.2 **AFM analysis of the fresh catalysts**

The topography of the untreated samples, as shown by AFM, is shown in Figures 6-2a to 6-2e. Figure 6-2a images the surface of the untreated Pd foil. Hollows are visible between long, parallel stretching features. The appearance of the surface of the foil is probably due to the polishing procedure used by the manufacturer. When the resolution was enhanced, a few narrow trenches in the surface, in no particular direction, became visible. These trenches are thought to be grain boundaries and will be discussed in greater detail later. No long-range order of any kind was revealed by AFM (regions of 140 x 140 µm² can be scanned with our equipment) for the two film samples. The surface merely consisted of a flat layer of palladium with irregularly shaped particles of various sizes on top of it (Figures 6-2b and 6-2c). The main difference between the thick and the thin films was the roughness of the surface, which is more pronounced on the thick film (by about one order of magnitude), which is due to the higher deposition rate during the preparation of the thick film sample. Figures 6-2d and 6-2e show two characteristic nanostructured samples: palladium dots (7 nm in height) on the silicon oxide layer and palladium (20 nm) deposited in the pits (60 nm in depth) of the oxide. The single palladium dots were well separated from their neighbors and have nearly the same size and shape. The arrays, formed from these ordered particles, cover the 4 inch wafers. Most of the dots investigated on the samples have a rough surface structure as presented here, which exhibits irregular features. It is not clear whether the small particles on top of the metal clusters are a result of the sputtering process and consist of palladium or whether these features were created during the lift-off and cleaning process after evaporation. If the latter is true, then they would consist mainly of carbonaceous, polymeric material from the photoresist. XPS spectra of both samples revealed a large amount of carbonaceous material on the surface (Table 6.1). However, a space-resolved investigation of the distribution of the various elements on the surface is difficult. The resolution of most scanning Auger microscopy equipments, which would be a promising tool for making this determination, is not high enough for such small particles.
Figure 6-2
Topography of the palladium model catalysts (as received/produced) as shown by AFM (3D presentation):

a) foil (40 x 40 μm²);

b) 500 nm film (10 x 10 μm²);

c) 10 nm film (10 x 10 μm²);

d) 7 nm dots (1.3 x 1.3 μm²);

e) 20 nm pits (1.4 x 1.4 μm²).
To clean and activate the contaminated model catalysts, oxidation and reduction treatments as described below were applied. These treatments are similar to the cleaning and activation processes used in industrial catalysis and were chosen because they indicated good results, as described in the foregoing chapter. Furthermore, the typical surface science methods such as sputtering or oxygen plasma etching have been tested to be less successful in removing the polymeric adlayers and it was reported that a silicon oxide layer formed on Pt particles when plasma etching was applied [Jac96].

6.3.2 Characterization of the catalysts after repeated cycles of oxidation at 400°C and reduction at 200°C.

All model catalyst systems were treated in a flow of oxygen and argon or hydrogen and argon in the quartz glass reactor described above. Overall flow rates were around 4 ml/min at a pressure of 10^5 Pa, the ratio between the argon and the second gas being 3:1 in all cases. The oxidation/reduction cycles were carried out in the following manner: First, the samples were heated to 200°C in the flowing Ar/O₂ mixture and kept at that temperature for two hours. The oxygen flow was stopped and the argon flow (3 ml/min) continued for 10 min. Then the gas flow was switched to the Ar/H₂ mixture at the same temperature. At that time, oxygen was still present in the reactor, which led to the formation of water on the Pd particles or films. The water was visible as it condensed on the cooler parts of the outlet tube and could be measured by the QMS. The reduction took two hours. This cycle was repeated three times, while the last oxidation was carried out overnight (usually 10 – 12 hours). After reducing the sample again at 200°C, the temperature was increased to 400°C under a flow of Ar/O₂. That temperature was maintained for 2 hours before the reactor was allowed to cool down to 200°C and the flow switched back to the hydrogen gas mixture. The reduction was always carried out at 200°C to avoid the formation of palladium silicide [Lom98] on the supported catalysts. This cycle was repeated at least twice. The catalyst then was removed from the reactor (at a temperature of around 80°C) and transferred immediately to the UHV chamber.
6.3.2.1 XPS and AFM analysis of the Pd catalysts after a redox-treatment at 400°C

Figure 6-3 shows the XPS spectra of the Pd 3d signals after the oxidation/reduction treatment. Minor changes in the peak area intensity were observed for the foil and the thick palladium film (500 nm), whereas the binding energies of the Pd 3d signals did not change. Therefore, any palladium oxide that formed during the oxygen treatment was reduced by hydrogen. The increase in the peak intensity was due to the removal of a significant amount of carbon-containing material from the metal surface during oxidation. The relative amount of carbon compared to the untreated samples was decreased by a factor of 4 (2) on the foil (film) (Table 6.1).

In contrast, significant changes in the binding energy of the thin palladium film (10 nm) as well as in peak intensity of the palladium and silicon signals were observed, whereas only the peak intensity of the nanostructured samples changed drastically. The Pd 3d signals of the thin film sample shifted from the metallic values observed for the fresh sample to values of 336.0 and 341.3 eV, which are the same values that were found for the palladium particles of the nanostructured samples. The higher binding energy in this case was not caused by changes in the chemical state of the palladium. If that had been the case, then the Pd on the thick film and the foil would have undergone the same changes after these treatments. Loss of metal due to evaporation from the surface to the gas phase did not occur because of the low temperature applied (400°C). Therefore, the drop in the signal intensity was due to the topographical re-arrangements of the palladium surface. The decrease in the intensity of the Pd 3d signal combined with a strong increase in the Si 2p peak at a binding energy of 104.1 eV led to the conclusion that the closed film of the fresh sample had reshaped to form isolated particles. The silicon oxide of the support was uncovered and the sample became insulating. AFM images of the sample (Figure 6-4c) show the formation of irregularly shaped isolated particles with uncovered substrate material between them. This effect is well known from investigations of MOS (metal-oxide-semiconductor) sensors [Erl91] and also from the production of supported noble metal particles from thin films on model substrates [Gun97], [Hen98].

Comparable effects caused a decrease in the intensity of the signal of the nanostructured samples. The effects on the pitted samples were discussed in the foregoing chapters; the explanation is similar in the case of the nano-dots. As can be seen in
Figure 6-3
XPS spectra of the Pd 3d signal of the model catalyst samples after oxidation and reduction treatments at 400°C:
a) foil; b) 500 nm film; c) 10 nm film;
d) 7 nm dots; e) 20 nm pits; f) 20 nm dots
Figure 6-4

Topography of the palladium model catalysts after oxidation and reduction treatments at 400°C as shown by AFM (3D presentation):

a) foil (40 x 40 μm²);

b) 500 nm film (10 x 10 μm²);

c) 10 nm film (3 x 3 μm²);

d) 7 nm dots (1.2 x 1.2 μm²);

e) 20 nm pits (1.4 x 1.4 μm²).
Figure 6-4d, the flat cylinders supported on the flat (non-structured) SiO₂ (Figure 6-2d) have reshaped to form small cones of increased height but with significantly smaller base radii. Some of the cones seemed to consist of one piece of metal, whereas most of the cones obviously consist of several crystallites. Even after scanning relatively small areas of the surface of the wafer, it was obvious that they were no longer uniform. Whereas some particles were smaller due to a loss of material, others were bigger as a result of the palladium migration processes induced on the surface. Therefore, two effects were responsible for the lower signal after the oxidation/reduction treatment: the formation of larger aggregates caused a decrease in the surface to volume ratio of the overall amount of palladium. Much more important, however, was the reshaping from flat cylinders to cones with a higher aspect ratio. This was proven best by simple geometry. All the deposited palladium films and particles discussed here were thicker than the information depth of XPS under the given conditions. Therefore, the signal intensity (peak areas) is directly related to the surface area that was exposed to the X-ray beam. In a first approximation, a cylindrical shape was assumed for the calculation of the surface of the flat disks (on the dot samples after preparation). The surface area of an ideal cone was assumed for the reshaped particles after the high temperature treatment. If the volume of a given dot is assumed to be constant, then the reshaped cone exhibits only around 34% of the surface area of the formerly flat cylinder. Therefore, the decrease in intensity, observed by XPS, can be explained by the loss of surface area due to reshaping and sintering of the particles.

The relative decrease in the intensity of the pitted sample was usually smaller than that of the flat samples. As stated above, the initial lower intensity of the Pd films in the pits was mainly caused by the large amount of carbon on the surface of these samples. After the oxidation and reduction cycles, the ratio between the intensity of the carbon and palladium signals was nearly the same on the pitted and the dot samples. Since the metal clusters in the pits could not change their position and, therefore, no sintering was observed, this loss is due solely to the reshaping of the clusters.

Except for the decrease in the intensity of the C 1s signal and, as a result, the increase in the intensity of the Pd 3d signal, the XPS spectra of the palladium foil and the 500 nm film showed no significant differences compared to the fresh samples.
Nevertheless, the topography of the two samples changed. This is most obvious in the case of the thick film sample (Figure 6-4b). The formerly random arrangement of particles with a broad size and shape distribution on top of a closed and flat layer of metal disappeared. The surface was instead divided into irregularly shaped, sub-micrometer-sized domains by deep narrow trenches. Since no charging effects and no signal contribution from the silicon oxide of the support were detected, the domains were assumed to be in close contact. The domains represent the nano-crystallites that were formed during the deposition of the growing film. The appearance of such features in the structure of thick evaporated or sputtered aluminum films after annealing is known from publications on semiconductors [Bec93]. Elevated features were visible at the “triple points” (where three or more boundaries meet). Such features are usually observed on metal films, which are doped with a second material, such as silicon. The temperature-induced reshaping of the films then leads to segregation of the doping material at the triple points of the grains of the host material. Since carbon was the only compound present in large amounts on the samples investigated, we suppose that the features contained a significant amount of carbon (silicon, originating from the wafer as a possible contaminant, was not detectable by XPS on the sample surface). This is in agreement with the intense C 1s signal observed on the sample after the treatments at 400°C. The amount of surface carbon was reduced by only a factor of 2, whereas on the other model catalysts the C 1s intensity was decreased by at least a factor of 4. Since the surface contamination of the sample by carbon was comparable to that of the thin film and the dot samples before any treatment but was much less than on the foil and the pitted samples, the remaining carbon probably separated from the bulk of the film and the palladium/silicon oxide interface and became attached to the surface. When the sample was exposed to oxidizing conditions for a longer period of time at higher temperatures, the amount of carbon decreased considerably (Table 6.1), which was again correlated with a change in the structure of the film (see next section).

Removing carbon from metals by combustion to CO₂ in the presence of oxygen has been discussed as a possible driving force for the restructuring of metal surfaces [Eri90], [Erl91], [Wei96]. The exothermicity of the formation of water from hydrogen and oxygen and the humidity inside the reactor during the high temperature treatments
can be excluded as reasons for the reshaping of the structured samples. The particles behaved the same when they were oxidized in dry oxygen at the same temperature of 400°C. For restructuring to occur under UHV conditions, temperatures above 550°C were necessary.

6.3.2.2 Behavior of structured Ag catalysts after redox-treatment at 400°C

For comparison, the changes in the topography of a silver dot sample before (Figure 6-5a) and after oxidation/reduction at temperatures up to 400°C (Figure 6-5b) are shown in Figure 6-5. The sample was prepared in the same way as the corresponding Pd dot samples, by evaporation of a silver layer of 10 nm. The dots in Figure 6-5a show a significantly rougher surface than the comparable Pd dots. After the oxidation and reduction cycles, the formerly well-ordered arrays disappeared almost completely (a comparable behavior of Ag dots prepared by electron beam lithography has been reported [Yan98]). The silver spread over the surface and covered the whole substrate with a grainy layer of small clusters. These clusters were only loosely bound to the surface. The lower corner of the sample imaged in Figure 6-5b was scanned several times by the AFM tip in contact mode, using rather high scan frequencies and high tip forces (7 to 8 nN). The scan area was then enlarged and the image recorded during the first scan. It is obvious that the silver in the small scan area was swept to the borders of the rectangular region. XPS spectra recorded on such samples (not shown here) after the oxidation/reduction treatments showed a higher Ag intensity than that on the freshly prepared dots, since the surface to bulk ratio was slightly increased. Figures 6-5c and 6-5d show a pitted sample, the pits filled with a 15 nm Ag film by evaporation, before and after the sample was treated with oxygen and hydrogen at 400°C. The surface structure of the Ag films inside the pits right after preparation (Figure 6-5c) is comparable to the structure of the dots in Figure 6-5a. Nevertheless, the walls of the pits prevented the metal from spreading over the entire surface, as was observed on the flat SiO₂ surface.
Figure 6-5

Topography of the silver model catalysts before and after oxidation and reduction treatments at 400°C as shown by AFM (3D presentation):

a) Ag dots (height 15 nm) on flat SiO2, untreated (3 x 3 μm²);
b) Sample as shown in a) but after oxidation/reduction cycles at 400°C (3.5 x 3.5 μm²);
c) Ag film (height 15 nm) on pitted SiO2 substrate (1.7 x 1.7 μm²);
d) same sample as in c) but after oxidation/reduction cycles at 400°C (1.7 x 1.7 μm²).

6.3.3 Oxidation of the Pd catalysts at 600°C.

The samples described above (except for the samples containing silver) were used for oxidation at 600°C. After oxidation and reduction cycles at up to 400°C and subsequent XPS and AFM investigations, the samples were transferred back to the glass reactor. After two oxidation/reduction cycles at 200°C and two cycles at 400°C, the temperature was increased to 600°C. The samples were kept in an argon/oxygen flow as described above. The temperature was steady for two hours, after which the reactor was cooled to 100°C in about 30 min without further reduction of the samples.
The samples were transferred immediately to the UHV system for further investigation.

6.3.3.1 XPS and AFM analysis of foil and films after oxidation at 600°C

Figure 6-6 shows the XPS spectra of the oxidized samples. The main peaks of the Pd 3d signal for the Pd foil (and the 500 nm film) were now located at 336.6 eV (336.5 eV) and 342.0 eV (341.9 eV). This indicated a heavily oxidized metal surface. Nevertheless, a clear shoulder at the lower binding energy side was observed, especially in the spectrum of the thick film. Deconvolution of the spectrum led to binding energies for the metallic palladium of 335.2 eV/340.0 eV (foil) and 334.5 eV/339.8 eV (film), indicating slight shifts to higher binding energy compared to the values obtained for the reduced samples. The entire outer metal surface area of the foil catalysts was oxidized in the reactor, thus causing an insulating oxide layer that covered all of the palladium foil, and therefore, shifted the signals to higher energy values as a result of charging. The effect was less significant for the thick film sample, where the amount of detectable Pd metal was comparatively larger (see peak in Figure 6-6). Furthermore, after oxidation of this sample at 600°C, a small Si 2p signal contribution by the SiO$_2$ layer was observed for the first time. Therefore, it was concluded that, at the higher temperature of 600°C, the thick evaporated metal layer underwent reshaping that was comparable to that of the thin film at 400°C. A first indication of this was already observed after the treatment at 400°C, when clearly separated grain boundaries were visible on the thick film sample.

However, the packaging of the domain areas was still very dense and no contribution by the SiO$_2$ to the XPS signal was observed after the treatments at 400°C. Increasing the temperature to 600°C led to a significant decrease in the amount of carbon detected on the surface (Table 6.1) and to a break-up of the formerly closed Pd layer (Figure 6-7b). The binding energies of the palladium in the metallic state and the AFM images led to the conclusion that none of the particles were completely isolated but that a coherent network of irregular shaped metal/metal oxide clusters was formed.
Figure 6-6
XPS spectra of the Pd 3d signal of the model catalyst samples after the oxidation at 600°C:
a) foil; b) 500 nm film; c) 10 nm film;
d) 7 nm dots; e) 20 nm pits; f) 20 nm dots.
Figure 6-7
Topography of the palladium model catalysts after oxidation at 600°C as shown by AFM (3D presentation, with the exception of the foil sample):

a) foil (40 x 40 μm²);

b) 500 nm film (4 x 4 μm²);

c) 10 nm film (10 x 10 μm²);

d) 7 nm dots (1.2 x 1.2 μm²);

e) 20 nm pits (1.3 x 1.3 μm²);

f) 20 nm dots (4 x 4 μm²).
There was a predominance of elongated and elevated parallel structures on the fresh foil, which were still visible after the treatments at 400°C but almost completely disappeared after oxidation at 600°C (Figure 6-7a). At the same time, the depth of the holes on the foil surface decreased significantly. Instead of the long-range, ordered, parallel structures that were probably due to the manufacturing process, the samples exhibited elevated structures, which formed the boundaries of large domain areas. These domains, however, were orders of magnitude larger than the small regions observed on the thick film sample after treatment at 400°C.

6.3.3.2 XPS and AFM analysis of the structured samples after oxidation at 600°C

The effect of high temperature oxidation on the structured samples is shown in the XPS spectra in Figure 6-6 and the AFM images in Figure 6-7. All the palladium particles were heavily oxidized according to peak shape and binding energy. The values for the Pd 3d doublets of both the pitted and the dot samples were 337.9 and 343.2 eV, respectively (again, the values were shifted to higher binding energies as compared to the foil and the thick film sample). Compared to the values observed for the same samples after reduction (336.0 and 341.3 eV), this is a shift of almost 2.0 eV, indicating that PdO was the predominant palladium species on the surface of the catalyst. All spectra of the structured samples showed low binding energy shoulders. Deconvolution led to binding energies of 336.2 and 341.5 eV for the palladium remaining in the Pd⁰ state. Only very few differences were found in the topography of the pitted samples and the 7 nm dot samples after oxidation at 600°C and the redox treatment at 400°C. Deviations in the height and width of the clusters were attributed to the lower density of PdO compared to Pd. The two dot samples, however, differed significantly from each other. The sample with the 7 nm dots still exhibited a well-ordered arrangement of the particles on the surface, and all the dots were split into small, conically shaped crystallites (Figure 6-7d), comparable to the structure after the O₂/H₂ treatment at 400°C (Figure 6-6d). The thick Pd dots (20 nm, Figure 6-7f) were more mobile on the surface and the particle surface appeared to be smoother after the high temperature oxidation. Note the difference in the lateral scale of the two images. For the purpose of comparison, the magnification factor in the z direction (height) was the same for both images. The arrangement of the thicker dots on the
surface was less regular than before the oxidation, and smaller features were visible between the regular positions of the dots. These features were randomly spread over the surface and were presumed to be traces of larger particles that moved around on the substrate. We do not yet know the causes of this behavior or why the larger particles were more mobile on the surface. (Note: the sizes of the metal dots investigated here differed in height, not in diameter. Therefore, the contact region between the metal and the substrate was the same for all of the dots.) However, comparable investigations of Pt particles, produced by electron beam lithography on CeO$_2$, showed disintegration of particles with diameters larger than 300 nm, whereas smaller particles crystallized into single crystals after coming into contact with a mixture of H$_2$/O$_2$ at 727°C [Joh99]. Therefore, the different behavior of ‘smaller’ and ‘larger’ metal particles on oxide surfaces may be due, among others, to the optimum surface-to-volume ratio, which is determined by the different materials involved (metal, oxide, adsorbates).

After the high temperature oxidation, all the samples described here were reduced at 200°C in a stream of an argon/hydrogen mixture in a further step for 2 hours. After this treatment, the binding energies of the Pd 3d signals of all the samples were the same as those which were determined after the oxidation/reduction steps at 400°C. The carbon-to-palladium ratios are given in the right column ('Redox 600°C') of Table 6.1. The topography of the oxidized and the reduced samples was slightly different, with the latter having nanostructured particles with a smoother surface. No obvious structural changes were observed for the foil and film samples after the additional reduction step.

6.3.4 Reactions carried out on the model catalysts.

As described above, the palladium-based catalysts were active towards the oxidation of hydrogen during the oxidation/reduction treatments. Since some parts of the reactor could not be heated, the water that formed during the experiments was visible as a condensed water film on the inner walls of these reactor parts. More reliable and comparable measurements of the activity for the formation of water were not possible, because the stainless-steel capillary that was used for connecting the reactor to the mass spectrometer showed high catalytic activity, too. Therefore, the
Comparison of Model Catalysts

capillary was removed from the reactor during the oxidation/reduction cycles. The pitted samples with palladium as the active material showed the best stability against oxidizing atmospheres at elevated temperatures. One of these samples was therefore used after the treatments at 400°C to test the catalytic activity for the CO oxidation.

Figure 6-8
Formation of CO₂ on a pitted Pd sample in a flow of Ar/CO/O₂ as a function of temperature (dashed line). Details are given in the text.

The sample was kept in a flow of 6 ml/min Ar and 2 ml/min CO at 10⁵ Pa and 300°C. When the flow of oxygen (2 ml/min) started, no CO₂ was formed at this temperature (Figure 6-8). Increasing the temperature to 350°C (dashed line) caused the catalytic reaction to start, showing oscillations. The temperature was then increased again to a maximum of 475°C. The maximum production of CO₂ was achieved already at a temperature around 360°C, with no major changes above this temperature. The empty reactor (without the catalyst but with the steel capillary) showed almost no activity towards CO oxidation. Therefore, the oxidation and reductions cycles, as described above, are appropriate for cleaning and activating model catalysts that have been contaminated by large amounts of carbon-containing
species. Contaminations of that kind are a typical problem of systems produced by lithography.

**6.4 Conclusions**

The influence of oxidation and reduction treatments on various model catalysts at high temperatures was investigated. We focussed on the topography and chemical composition (the oxidation state of the active material and the number of contaminants on the surface) of the model systems which all were prepared under very similar conditions. The long-term oxidation and reduction cycles proved to be appropriate cleaning and activation procedures, even for catalysts that were produced by lithography and were, therefore, contaminated by carbonaceous adlayers. Carbon-containing contaminants were burned off the surface, leading to catalytic active metal surfaces. The metal foils, films, and structured particles showed significant restructuring of the surface and the "near-surface" bulk. Defined and reproducible restructuring without sintering was only observed on the pitted samples. Some of the results that relate to major restructuring and oxidation/reduction behavior are not new. However, if we focus on the exact behavior of systems with defined system properties (e.g., particle size, particle arrangement, purity, and chemical composition), the investigation showed that further research must involve more than the simple evaporation of metal films on flat substrates. The etching of the active species (films or particles) exposed to elevated temperatures and reactive conditions (described as thermal and catalytic etching in the literature [Wei96]) depends strongly on the properties of these materials. Therefore, when the size, shape, bulk, and surface composition differ from one system to another, it is not surprising that the results of catalytic investigations on nearly identical systems are contradictory. Chemists working in the field of catalysis know that the performance of a given catalyst depends strongly on the method of production and on pre-treatment. The pitted samples presented here as nanostructured catalysts are remarkably stable against 'long-range etching' (i.e., mobility of metal particles on the oxide surfaces leading to sintering). Therefore, they can be treated in an identical manner as actual metal catalysts used in industry that are supported on powdered, porous substrates.
7. Silver model catalysts prepared on pitted SiO$_2$ surfaces

7.1 Introduction

Silver is used as a catalyst for a number of industrial partial-oxidation reactions. The epoxidation of ethylene and the synthesis of formaldehyde have attracted far more attention. Despite the widespread use of silver in heterogeneous catalysis and numerous investigations of the elemental steps of the reactions, only little is actually known about the detailed mechanisms and the changes induced in the active silver phase during the reactions. It was reported recently [Nag99] that almost none of the numerous surface science studies available took the effort to observe the morphological changes in the catalyst during or after exposure to oxygen at elevated temperatures. In addition to a wealth of single-crystal studies on Ag (110) and Ag (111) surfaces and on polycrystalline silver foils (references can be found in [Bei94] and [Nag99]), only few “realistic” catalyst models (silver clusters supported on flat oxide supports) have been investigated so far [Ara84], [Bei94], [Ruc84]. This may be due to weak metal-support interactions between the silver and the oxide supports, which are in the range of Van-der-Waals interactions. Model calculations for Ni and Pt clusters on alumina supports showed repulsive forces between the occupied O$^-$ orbitals and the almost filled d-orbitals of the noble metals. Experimental proof of the weak anchoring of evaporated silver particles on oxide surfaces like Al$_2$O$_3$ and SiO$_2$ resulted from AFM investigations of such systems. Imaging of thin films or small particles right after evaporation was not possible in contact mode, because the forces between the scanning tip and the cluster were larger than the cluster-support interactions. Only after UHV annealing of the systems and applying tip forces below 0.8 nN was it possible to image isolated silver clusters on the single crystalline Al$_2$O$_3$ surface [Bei94]. XPS investigations of the same samples showed that the silver particles already had undergone sintering under the annealing conditions. Even after annealing, it was possible to move the clusters along the terraces of the oxide crystal by the scanning tip (see also Chapter 6.3.2, Figure 6-5a).
Therefore, the poor stability of supported silver model catalysts may explain the lack of detailed investigations of the effect of size, structure and morphology of supported silver particles on the catalyst properties during partial oxidation reactions. This chapter describes the use of nanostructured supports for the preparation of supported silver catalysts. The stability of the arrangement of the supported silver particles improved considerably, whereas on flat supports sintering and redispersion occurred under the reaction conditions.

7.2 Results and discussion

7.2.1 Pitted samples with evaporated silver inside the pits

Preparation and analysis of the silver model catalysts were described in Chapter 6. In addition to the standard procedures described thus far, silver films were evaporated onto flat and structured (pitted) surfaces after removing the photoresist. Subsequently, the films were annealed and the behavior of the silver layer observed by AFM.

Chapter 6.3.2 reported changes in the topography of silver films (10 nm thick), evaporated through the structured resist into the pits of a silica surface, after oxidation/reduction treatments at 400°C. The films showed a rough surface morphology after evaporation, and they reshaped during the annealing procedure. Contrary to comparable palladium samples, several spherical silver particles were found in a single pit after annealing.

Comparable results were obtained after UHV annealing of the samples. Figure 7-1 shows the AFM image of a pitted sample with 15 nm of evaporated silver inside the pits, after 5 min at 500°C in UHV. In contrast to the results for palladium (Chapter 4), the films already reshaped at this temperature to form 3D particles at the bottom of the pits; small regions of the flat, smooth, silica bottom are visible between the clusters. The average diameter of the particles was 75 nm, and the average height was around 30 nm (measured from the visible areas at the bottom of the pits to the tops of the particles). However, due to the formation of several small clusters instead of one large particle, the surface area relative to the particle volume was not that much
smaller. Therefore, no decrease in the XPS intensity of the Ag 3d signals relative to the Si 2p peak was observed, as shown in Figure 7-2.

However, this changed significantly after exposing the samples to temperatures above 600°C. Depending on the amount of deposited silver and on the temperature and pressure during the annealing, much less or even no silver was left on the surface, even after short annealing times of 10 min. A significant increase in the vacuum chamber pressure was observed when the silver samples were heated to 650°C in UHV, although the evaporation rate of silver metal as dependent on the vapor pressure should be quite low at that temperature. However, Sambles et al. reported that the rate of evaporation of Ag increased considerably in the presence of contaminations and/or small amounts of water [Sam70]. Nagy [Nag99] observed a change in the color of SiO2 pellets, supporting Ag particles, from white to gray after running the oxidative coupling of methane as a test reaction in a quartz tube reactor at 800°C. The analysis revealed the presence of carbon and silver in the formerly silver-free SiO2 pellets. This, too, suggests the sublimation of the silver from small supported particles under actual catalytic conditions and temperatures far below the melting point of the bulk silver. In closely packed catalyst beds, most of the silver is re-deposited in cooler parts, whereas on the flat samples described here, the silver is removed permanently from the surface.
Figure 7-2

XPS spectra of the Ag 3d peak of the sample shown in Figure 7-1. The intensity after the UHV annealing (- △ -) was identical to the intensity of the samples as prepared (- ○ -), when the annealing temperature was below 600°C. Annealing at 650°C for 1 min led to a significant decrease in intensity due to sublimation of the Ag (- ◊ -).

Using thinner films of the evaporated silver initially led to fewer and smaller particles after annealing the samples. Figure 7-3 shows a sample with 1.1 nm of evaporated silver after the lift-off procedure (a) and after annealing the sample for 5 min in pure oxygen at $10^5$ Pa and 400°C (b). There are only few small features in the pits after evaporation. Measurable heights of isolated particles range from 4 to 10 nm, whereas other regions on the bottom of the pits are completely free of silver. While 13% of the surface of samples with 15 nm of evaporated silver (as determined by XPS) was covered with silver, comparable measurements gave a coverage of 4% in case of the thin film (1.1 nm). There were even fewer particles on the surface after oxidation, most of which were still inside the pits (b). It is difficult to determine the exact size of the annealed silver clusters. However, the dimensions increased by at least one order of magnitude. Therefore, it is concluded that the small isolated
structures (Figure 7-3a) sintered to form single clusters (Figure 7-3b). However, the size and morphology of the clusters varied widely.

![Figure 7-3](image)

**Figure 7-3**

a) Three-dimensional view of a 1.8 x 1.8 μm² AFM image of a pitted sample with 1.1 nm of evaporated Ag in the pits.  

b) Detailed view of the sample shown in a) after annealing at 400°C in flowing O₂/Ar (1:1) at 10⁷ Pa (0.7 x 0.7 μm²).

### 7.2.2 Pitted and non-structured samples with evaporated silver films

The deposition of thin metal films onto oxide substrates by evaporation and annealing of the resulting systems is widely used to produce model catalysts (see Introduction and [Hen98]). However, as mentioned above, these particles have a broad distribution of size and it is almost impossible to achieve a well-defined arrangement of the clusters on the surface. Structuring the surface using methods described above helps to improve the uniformity of the clusters and enables the creation of a predefined pattern of metal particles on the flat surfaces. However, some contamination of the metal by carbonaceous species must be taken into account. Furthermore, the lift-off procedure requires a large amount of material, and the largest part of the expensive noble metal film is lost.

The enrichment of metal clusters at defective sites such as steps, kinks, and edges of flat supports after depositing thin films on oxide supports is well-known for
systems with only weak metal-support interactions. We used the well-defined arrangement of artificial defects (pits) on the flat silicon oxide surfaces to influence the formation of particles during the annealing of thin silver films.

Figure 7-4 shows two examples of the resulting model catalysts. Four nm of silver were evaporated onto heavily oxidized silicon wafers in both cases. The oxide surface in Figure (a) was structured to give a pitted surface, whereas the sample in Figure (b) was taken from an unstructured wafer. Nevertheless, both samples were covered by photoresist and had been in contact with the etching solution. After etching and the removal of the resist, both samples were treated in a stream of oxygen at 400°C and 10^5 Pa for several hours before the silver was deposited in order to remove as much of the remaining resist as possible. After evaporating the metal, the samples were annealed in a stream of pure oxygen at 10^5 Pa and 450°C for 10 min. The procedure is comparable to routines applied in the manufacture of silver particles on glass slides, which are used to investigate SERS effects (Surface Enhanced Raman Scattering) [Stö99]. The silver particles are arranged randomly on the flat surface.
(Figure b), whereas the particles on the structured surface (Figure a) fill the pits and, therefore, resemble the arrangement and diameters of the pits. Further annealing in UHV or under the same conditions as described above led to no further changes in the morphology of the samples. The particle size distribution is rather broad in both cases. The advantage of the well-ordered arrangement of the clusters on the structured substrate is somewhat diminished by the larger particles. The heights of the clusters (measured from the level of the flat silicon surface) ranged from 20 to 55 nm, and the diameters varied from 340 to 360 nm, whereas the particles on the flat surface were 20 to 40 nm high and had diameters between 100 and 180 nm. Decreasing the diameters of the pits and using thinner evaporated films should lead to smaller metal clusters.

The surface structure shown in Figure 7-4b is surprising, when compared with that of the sample shown in Chapter 6.3.2, Figure 6-5b. In the latter case, a silver dot sample (silver clusters prepared by lithography on a flat, unstructured silica surface) was treated for several hours in oxygen and hydrogen at 400°C and atmospheric pressure. Despite the similar treatments, the resulting morphology, i.e. the size and distribution of the silver clusters, was very different. Thus, even the metal-support interactions between the silver and the silica were much weaker than on the samples presented here. The reasons for this different behavior are not yet clear. It is suggested that the different pre-treatments of the support and the resulting variations in the surface composition of the support and the metal clusters play an important role. Furthermore, the dot sample presented in Chapter 6.3.2 was exposed to oxygen and hydrogen during annealing. Therefore, small amounts of water formed on the metal parts of the glass reactor, leading to humidity in the tube, whereas the oxygen used in these investigations was completely free of water. These contrasting results for both types of samples and annealing conditions are reproducible; thus, the different behavior must be due to the different annealing conditions.

7.3 Conclusions

Little is known about the behavior of supported Ag particles that are exposed to catalytic conditions, perhaps because of a lack of appropriate, stable model systems. It
was shown that the behavior of small silver clusters and thin films, which were deposited on flat silicon oxide layers, were significantly influenced by the morphology and chemical composition of the substrate. The performance of a catalyst is usually based on the entity of its components; thus, the importance of "realistic" model systems must not be underestimated. The increase in the rate of sublimation of silver from supported silver clusters compared to the bulk silver of single crystals or foils is only one significant indication of the effect of the interactions between the active phase of a catalyst and its surroundings.

Furthermore, silver is widely used as a substrate for UV-VIS extinction spectroscopy and for Raman spectroscopy investigations [Dec98], [Gun99], [Jen99] due to its unique optical and electronic properties. After gold, copper, and aluminum, it is one of the most common metals used in IC technology. In all these research fields, detailed knowledge of the behavior of small amounts of metal (clusters or thin films) in contact with one or more different materials (e.g., wetting behavior, reconstruction, epitaxy, alloy formation) is essential.

The use of structured supports with well-defined properties, as described here, offers good opportunities for such studies.
8. Concluding remarks

8.1 Nanotechnology and catalysis

The detailed observation of catalytic processes by means of modern surface science techniques has aided our understanding of catalytic mechanisms on a molecular level. To increase this knowledge, however, simplified model systems that closely resemble industrial catalysts must be developed for basic research in catalysis. Therefore, cheap and efficient methods for the production of submicrometer- to Ångstrom-sized particles on flat support materials are highly desirable. A number of methods are available for producing highly defined metal-particle arrays on flat support materials. Recent developments in the microelectronic industry, including electron-beam lithography and thin film deposition techniques, have contributed to the fast development of new and sophisticated model catalysts. Although the features produced that way are much larger than the size of the particles in most heterogeneous catalysts, the systems have a number of excellent features (well-defined individual clusters on the nanometer scale, accessibility by surface science methods and high reproducibility). In view of the progress made in miniaturization and the complexity of small-scale circuits in IC technology (aided by progress in computer technology) in the last few decades, it seems to be worthwhile to continue the attempts for bridging the remaining gaps between catalysts used in industry and the model catalyst systems available today.

8.2 The contribution of this work to the development of model catalysts

We succeeded in developing new model catalysts by means of laser-interference lithography. The method enables the fast, convenient production of low cost model catalyst systems with submicrometer-sized features on 4 inch wafers. The systems discussed here provide an ideal combination of structured topography (mimicking porous and powdered supports), high stability even under catalytic conditions, and
easy accessibility by a variety of surface science methods. Controlled deposition of metallic particles onto a nanostructured silicon oxide surface was achieved. The evaporation of palladium or silver through a patterned resist into pre-etched pits as well as the (more realistic) wet chemical method of copper and palladium by spin-coating precursor solutions led to perfectly ordered arrays of metal clusters with predictable sizes. A wide variety of support materials and metals can be used, once the system has been installed. Silica as a support material in combination with palladium, silver, and copper as active metal compounds has been described in this thesis.

Detailed investigations of the chemical composition and topography of the catalysts were carried out by means of electron spectroscopy (XPS), scanning probe microscopy (AFM, SEM), and mass spectrometry. The behavior of the systems, after being treated thermally (UHV annealing) and thermo-chemically (reactive gas annealing) (the treatments are also described as thermal and catalytic etching), was compared to standard model catalyst systems such as metal foils, thin films, and nanostructured metal clusters on flat silica surfaces.

Compared to most model systems known thus far, our arrays offer a unique combination of uniformity, stability, reproducibility, and large metal surface area. The otherwise flat silicon oxide layers on oxidized 4 inch wafers had $10^9$ to $10^{10}$ active metal sites. Therefore, the catalysts provide sufficient metal surface area for reaction studies, even at atmospheric pressure. Thus far, hydrogen and carbon monoxide oxidation have been active on the Pd systems after long activation and cleaning treatments. Cleaning and activation steps can be carried out according to procedures used in the actual preparation of catalysts at high pressure and high temperature, without disturbing the ordered arrangement of the individual metal clusters. It was shown that the stability of the pitted samples is significantly higher than that of evaporated particles located on a flat silicon oxide surface. Therefore, the restructuring of the metal clusters can be observed without the disturbing effects of sintering.
8.3 Further possible advantages of the pitted surfaces

The described systems offer many possibilities for research related to surface and materials science, not only in the field of catalysis. The wetting behavior of various metals on a variety of support materials at extremely high temperature and in various gas atmospheres can be studied in detail. The role of interfaces and contact regions can be determined by employing multi-layered systems with defined sequences of material (i.e., support/metal/promoter). The spin-coating method enables a more detailed investigation of the essential steps of catalyst production using wet chemical methods without the problems related to sintering at elevated temperatures. Finally, the mechanisms involved in alloying and the properties of the resulting composites can be investigated by evaporating two or more metals into the pits and then annealing them. Therefore, these samples may contribute to the ongoing research in combinatorial chemistry and catalysis (see [Jan98], [Wei98], [Con99], and [Jan99], for example).

Although much work remains to be done (e.g., improving the uniformity of the clusters and the purity of the systems, designing reactors that are more suitable for flat samples), the pitted samples offer a unique possibility for investigating isolated particles that interact only with the surrounding substrate and the reactive gas atmosphere. Changes in catalytic performance can then be traced back to a single microscopic particle instead of to the changing bulk sample. However, the development of analytical tools is not keeping pace with the ongoing trend toward the miniaturization in building nanowires, nanoclusters, and quantum devices. While it is possible to arrange single atoms in predefined patterns on surfaces and image the topography of surfaces with atomic resolution, only few analytical tools for elemental or even molecular analysis with comparable high spatial resolution are available. Surface-sensitive techniques with extremely high depth resolution (down to monolayers) like SIMS (secondary ion mass spectrometry) and SAM (scanning Auger microscopy) usually have only limited lateral resolution to a few micrometer and are restricted to UHV conditions.

The laboratory of Prof. R. Zenobi (Laboratory for Organic Chemistry, ETH Zürich) has a scanning near-field optical microscope with which near-field Raman spectroscopy can be done on a few molecules [Dec98]. This group is attempting to
build a reactor cell around the microscope. The catalytic performance of the catalyst would then be monitored by mass spectrometry or gas chromatography, while the microscope would yield information about molecules adsorbed on the clusters and about changes in the topography, all in a single experiment, carried out under realistic conditions.
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9. Literature


Publications:

“Foil films, and nano-structured surfaces: A comparative XPS and AFM study of model catalyst surfaces”
M. Schildenberger, Y.C. Bonetti, and R. Prins
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M. Schildenberger, Y.C. Bonetti, and R. Prins

“Nanotechnology and Model-Catalysis: The Use of Lithography for Creating Active Surfaces”
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Presentations at Conferences

“Nanohollows: Model heterogeneous catalysts built with interference lithography followed by metal deposition”
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“Investigation of size effects in heterogeneous catalysis using nanostructured (multilayer) systems”
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Abstract published: Chimia 51 (1997) 643

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