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Nanotechnology and Model Catalysis: The Use of Photolithography for Creating Active Surfaces

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Abstract: New and very stable model catalysts have been developed. Two types of samples on oxidized 4-inch wafers were produced using processes that are generally employed in semiconductor device technology. A single wafer exhibits 10^9 to 10^{10} active sites on an otherwise flat silicon oxide surface. Sputter etching of a number of bilayers (Pd/SiO₂), stacked on an oxidized Si wafer surface resulted in billions of isolated towers, consisting of disks of active metal layers, separated by inert substrate material. A second system was produced by etching pits into a heavily oxidized 4-inch Si wafer. Active material was deposited into the pits by e-beam evaporation or spin-coating of precursor solutions. The topography and chemical composition, and the changes induced by the reaction conditions applied, including stability and chemical behavior of the nanostructured systems, were investigated by means of AFM, SEM, temperature-programmed methods and XPS.

Keywords: COST · Model catalysis · Nanotechnology · Photolithography

Introduction

The detailed observation of catalytic processes by the use of modern surface science techniques will add to our understanding of catalytic mechanisms on a molecular scale. This knowledge, however, is difficult to obtain, because actual catalysts consist of poorly defined systems where the active noble metal species is located in the pores of a powdered support (silica or alumina, for example). Due to this complexity of heterogeneous metal catalysts there is a strong need for the development of simplified model systems for basic catalyst research. Despite the simplifications, these models should be as close as possible to industrial catalysts in order to deliver relevant data about the actual processes. Numerous attempts have been made to produce highly defined metal-particle arrays on flat support materials that would fulfill the innumerable demands on an ideal heterogeneous model catalyst. Any technique applied must at least satisfy two requirements, which are somehow contrary. Particles of predictable and variable sizes from some Ångströms to a few nanometers are necessary, and a huge number of identical particles has to be produced in short periods of time. Therefore, parallel production methods for cheap and fast production of submicrometer-sized particles are highly desirable.

Recent developments in the microelectronic industry aim to fulfill the same requirements, although the dimensions of the features in computer chip production nowadays are still too large to be directly compared to particle sizes demanded in most heterogeneous catalysts. However, highly sophisticated methods, such as photolithography [1] and e-beam lithography [2], produced catalysts with a number of excellent features (including well-defined individual clusters on the nanometer scale, accessibility by surface science methods and high reproducibility). Further developments will help to bridge remaining gaps. We have succeeded in developing new and very stable model catalysts by the use of laser interference lithography. Two types of samples, 'Nanotowers' and 'Nanopits', containing 10^9 to 10^{10} active metal sites on an otherwise flat silicon oxide surface on oxidized 4-inch wafers were produced using lithographic processes. The systems showed remarkable stability when exposed to high temperatures and reactive gas atmospheres.

Results

Laser interference lithography and etching techniques were used to create the patterns of both systems. The method takes only a few minutes and results in particles of submicrometer size and spacing that cover a 4-inch wafer. The beam of a He–Cd Laser was split and the two resulting beams were guided to give an interference pattern. Specially prepared wafers, covered with photo resist material, were double exposed to this pattern. The surface was then structured by etching the wafers through the resulting resist grid.

The 'Nanotowers' model catalyst system was produced by sputter etching of a number of bilayers (Pd/SiO₂), stacked on an oxidized Si wafer surface. Since two different materials have to be etched, wet chemical etching is not suitable for the creation of the nanotowers. The etching results in billions of isolated towers, consisting of disks of active metal layers, separated by inert

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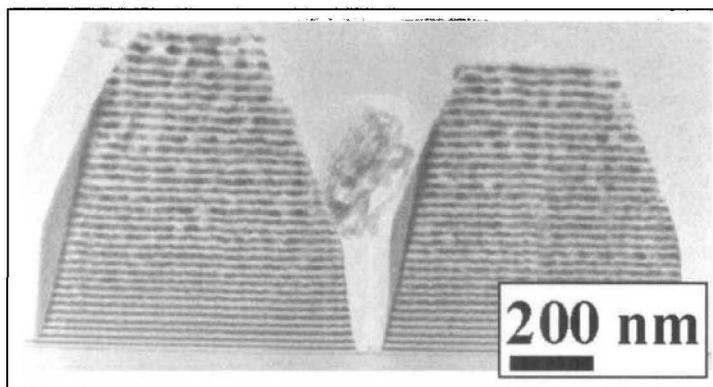


Fig. 1. TEM image of etched multi-layers (40 bilayers of SiO_2/Pd) on an oxidized Si wafer (visible at the bottom of the image). SiO_2 appears bright, Pd dark in the transmission image

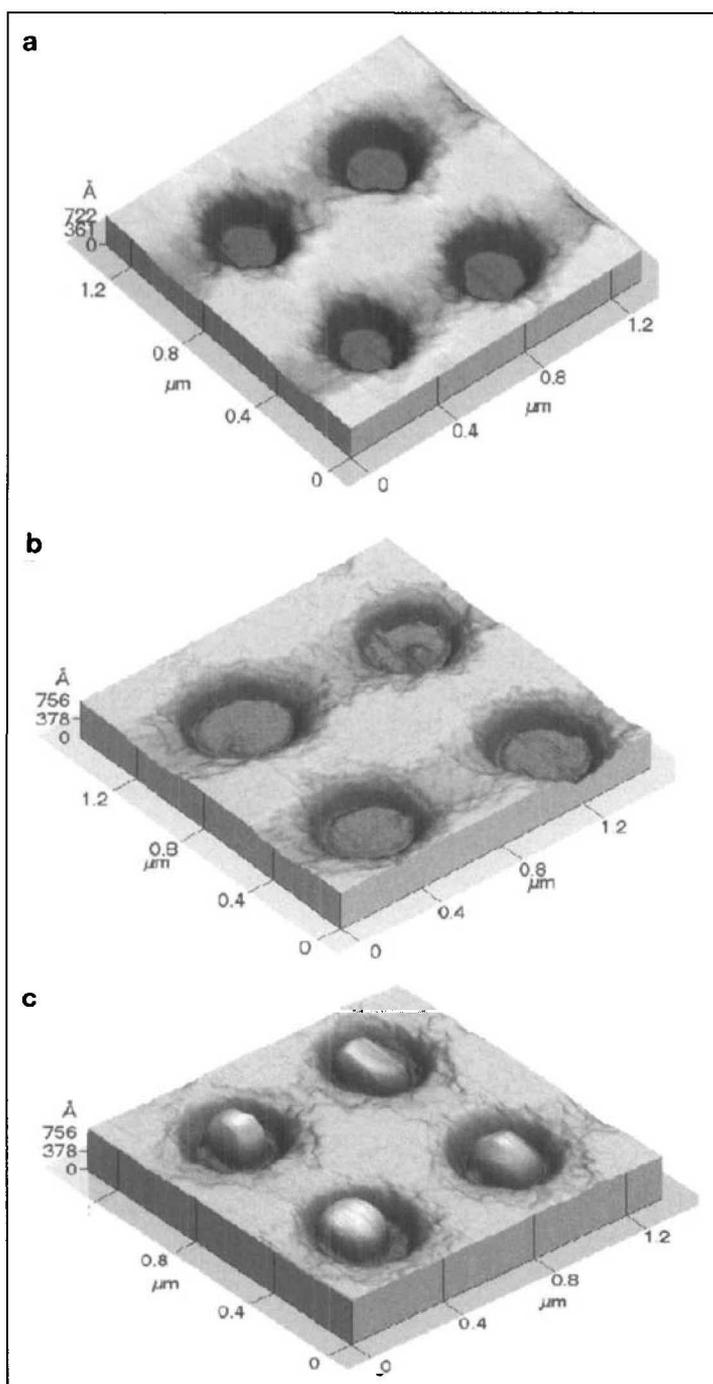


Fig. 2. 3D presentations of AFM images ($1.3 \times 1.3 \mu\text{m}^2$) of a nanopitted sample. Images show the sample after etching and before Pd evaporation (a), with 20 nm of evaporated Pd in the pits before (b) and after (c) annealing at 700°C in UHV.

substrate material. Two examples of such towers are presented in Fig. 1. 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.

The 'Nanopits' catalyst system was created by wet chemical etching of a heavily oxidized wafer surface through a structured resist layer. The produced pits (Fig. 2a) were subsequently filled with metal by evaporation (Fig. 2b) [3][4]. The metal films inside the pits then can be restructured to spherical particles by annealing in UHV or other atmospheres. The size of the spheres is controlled by varying the initial thickness of the metallic layer. Fig. 2 shows a sample after the various preparation steps. Significant changes in the structure of the particles can be observed. Fig. 2c shows an AFM image of a sample after UHV annealing at 700°C . The formerly flat, disklike films (Fig. 2b) reshaped to hemispherical particles but were still trapped inside the pits. Therefore, even at the high temperatures applied, no particle-particle sintering was observed. The same results were observed after treating the samples at 400°C and 600°C in oxygen. Calculating the volumes of the disks before and those of the hemispheres after annealing results in constant values for both shapes. This leads to the conclusion that no material was lost as a result of evaporation or due to losses through the diffusion of material into the bulk.

Starting with deposited films of 20 nm thick (Fig. 2b), the annealed particles are typically 45 nm high and about 200 nm in diameter. Evaporation of smaller amounts of material leads to smaller clusters, as was shown in the case of silver deposition. The evaporation of metals under high vacuum conditions is not necessarily comparable to the usual wet chemical impregnation techniques used in catalysis. This cannot be neglected, since structure, morphology, and catalytic properties are often strongly influenced by the method of preparation. However, the pitted samples as shown in Fig. 2a can be used for metal deposition by the spin-coating method. A drop of metal salt solution is added to a rotating wafer [5]. The sample is then calcined and reduced according to synthesis of 'real world catalysts'. Optimizing the parameters of the production procedures results in a single metal cluster arrangement (Fig. 3). The metal cluster at the bottom of the pit in Fig. 3 has a diameter of 80 nm and a height of 10 nm. The pitted catalysts (with evaporated Pd) were active towards the oxidation of hydrogen during oxidation/reduction treatments carried out in a specially designed quartz glass reactor. 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 to test the catalytic activity for the oxidation of CO. After several oxidation and reduction treatments at 400°C , the sample was kept in a flow of 6 ml/min Ar and 2 ml/min CO at 10^5 Pa and 300°C . When the flow of oxygen (2 ml/min) was started, no CO_2 was formed at this temperature (Fig. 4). Increasing the temperature to 350°C (dashed line) caused the catalytic reaction to start, showing oscillations. The temperature was then increased to 475°C . The maximum production of CO_2 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 reduction cycles are appropriate for cleaning and activating model catalysts that have been contaminated by large amounts of carbon-containing species. This is a typical problem of systems produced by lithography.

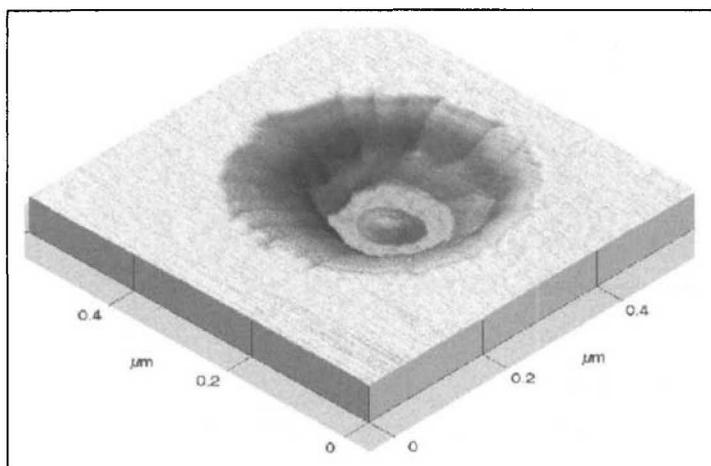


Fig. 3. AFM image (3D presentation, $0.6 \times 0.6 \mu\text{m}^2$) of a sample, spin-coated with $\text{Cu}(\text{NO}_3)_2$ solution, after annealing at 350°C in UHV

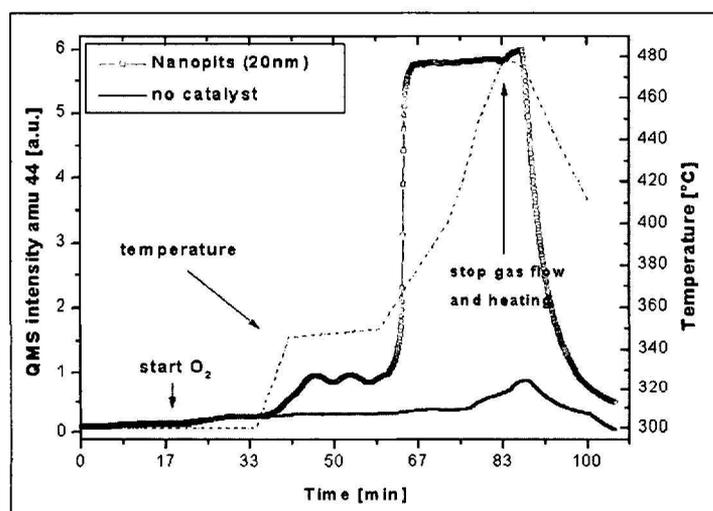


Fig. 4. Formation of CO_2 (mass spectrometry signal of amu 44) on a pitted Pd sample in a flow of Ar/CO/ O_2 as a function of temperature (dashed line)

Conclusions and Outlook

We produced new model catalysts by means of laser-interference lithography. Three different systems were introduced, which provide an ideal combination of structured topography (mimicking porous and powdered supports) and easy access due to a variety of surface science methods. Controlled deposition of metallic particles onto a nanostructured silicon oxide surface was achieved. 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. 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. The large number of catalytically active sites as well as the mimicking of actual impregnation of

such systems will help to bridge the material and pressure gaps in model catalysis. As with all lithographic methods, a wide variety of support materials and metals can be used after the process has been installed. Silica as a support material in combination with palladium, silver and copper as metals has been described. Current investigations focus on the use of alumina wafers as support material. Thus far, hydrogen and carbon monoxide oxidation have shown activity on the Pd systems after long activation treatments.

The etching of multilayered structures led to isolated towers with high aspect ratios. This way, the amount of catalytically active area on a single 4-inch wafer can be increased significantly due to the extension of the system in the third dimension. However, the contamination problems due to redeposition of the sputtered material have to be solved before the towers can be used for catalytic investigations.

The systems described offer many possibilities for research related to surface science, not only in the field of catalysis. The wetting behavior of various metals on a variety of support materials at extremely high temperatures and in different 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 in catalyst production using wet chemical methods, without difficulties 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 process in combinatorial chemistry.

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