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Local deposition and patterning of catalytic thin films in microsystems

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Abstract

The local deposition of catalysts is desired in a wide range of catalytic microsystems (microreactors and sensors). In this study, we investigate technologies enabling deposition and patterning of catalyst thin films in a manner compatible with standard micromachining processes. We evaluate and compare deposition techniques based on a combination of a self-assembly, soft-lithography and conventional micromachining. Platinum (Pt) and palladium (Pd) were used as model catalysts, both as a sputtered thin film and as nanoparticles supported on γ -alumina. The thin films were characterized and tested in terms of their catalytic activity based on CO chemisorption measurements, stability and reproducibility.

(Some figures may appear in colour only in the online journal)

1. Introduction

1.1. Role of catalyst

In catalytic microsystems, such as microreactors [1, 2] and combustible gas sensors [3], a catalyst is an important structural element in making the response of the system specific for the target molecules. The measured output of such systems depends on the chemical reaction occurring on the catalyst surface. The reaction is controlled by the temperature and the kinetic properties of the selected catalyst (e.g. activity, selectivity, stability). A catalyst reduces the activation energy for a reaction without being consumed. As the reaction takes place at the surface of the catalyst, it also fixes the location where an effect may be actuated or detected by a transducer. For this reason, the local deposition of a catalyst on micromachined surfaces is an important issue.

Pt and other noble metals (gold [4], palladium [5], rhodium [6]) are well-established catalysts for partial and deep oxidation of hydrocarbons [7–9]. Pt and Pd are often applied as model oxidation catalysts due to their ease of use, and a large number of publications reporting kinetic data are available.

The ability of Pt and other noble metals to lower the activation energy of many oxidation reactions makes it a useful catalyst in catalytic microsensors [10] and in catalytic converters of automobile exhaust [11], as lower temperatures are required. The main reasons for this are high activity and high resistance to over-oxidation and poisons, such as sulfur, that can cause catalyst deactivation.

Bulk noble metals have, however, poor catalytic properties. To retain a catalyst's long-term stability, highly porous catalyst supports are often implemented, which have high catalyst dispersion and, therefore, resist the sintering of small active particles to inactive metal clusters.

In this study, different methods to deposit Pt- and Pd-based catalysts are applied. The catalysts were deposited as solid thin films and as nanoparticles dispersed on a highly porous alumina. The first method has the advantage of deposition and patterning in a straightforward way: by using a combination of thin metal deposition (evaporation or sputtering), traditional UV lithography and metal lift-off or wet etching. These deposition techniques are compatible with the processing of the sensor system. Post deposition, the catalyst can be used subsequently without an activation procedure.

Supported catalysts require the development of more sophisticated deposition techniques which need to be adapted to a specific microsystem design. Some of the techniques for high-resolution, low-cost patterning of ceramics from wet precursor have been reviewed by ten Elshof *et al* [12]. In addition, sol–gel-based catalysts cannot be used for sensing directly, but need to be activated at high temperatures (above 400 °C) prior to sensor utilization. The thermal activation procedure is not always compatible with materials comprising the sensor. The high surface area porous catalysts ensure a higher conversion and a lower sensitivity to deactivation. The response of such a system may be limited by diffusion times of gas molecules into the pores of the catalyst support containing active metal particles. However, if the catalyst film has a thickness up to a few micrometers and contains mesopores, the diffusive process is sufficiently fast, which is required for fast sensor response. From the approximated equation (1) for diffusion time (t), given the diffusion coefficient for propane $D = 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and the diffusion length equal to the thickness of the porous catalyst film $l_{\text{dif}} = 1 \text{ }\mu\text{m}$, times needed for propane to diffuse are in the order of 100 ns:

$$t \sim \frac{l_{\text{dif}}^2}{4D}. \quad (1)$$

1.2. Specifications of the catalyst and catalyst deposition

The choice of a catalyst is application specific and determined by the combination of catalyst and feasibility of techniques for local deposition and patterning. Generally, the following factors limit the degree of catalyst applicability and therefore are important:

- high activity;
- resistance to over-oxidation, poisoning and sintering;
- compatibility of the catalyst activation procedure with the materials of the sensor or microreactor;
- applicability of the deposition method at the microscale for local deposition and patterning (a catalyst pattern distributes mechanical stress induced at high temperature).

When applied in catalytic sensors, the activity of Pt has an impact on the heat generated and the operating temperature of the sensor. Although Pt is a good catalyst for a wide range of hydrocarbons, some degree of selectivity can be achieved based on two measurables: ignition temperature and heat release [13].

Pt is known for being resistant to deactivation at high temperatures. This gives a long lifetime and stability of the sensor when operated in an aggressive and (or) oxidizing environment. Pd is an alternative catalyst, but is more prone to oxidation.

Often, prior to utilization, the catalysts need to be activated which is achieved by heat treatment (calcination, reduction at temperatures above 300 °C) in a hydrogen containing ambient. This high-temperature annealing step has to be compatible with the materials comprising the sensor.

Technology must ensure proper operation of both the sensor and the catalyst afterward, and prioritize local positioning of the catalyst pattern in a reproducible manner.

1.3. Deposition techniques

To ensure a specific interaction between the gas analyzed and a sensing interface (micro hotplate), a catalyst is immobilized. One of the most critical factors is the development of a technology for local immobilization of the catalyst (or catalyst pattern) close to the transducer.

The deposition of thin catalyst films can be achieved using evaporation or magnetron sputtering. There is, however, no standardized approach for immobilization of sol–gel-based catalytic materials. The development of techniques enabling integration of sol–gel catalysts is important as they are commonly used as functional coatings in micromachined gas sensors [14] and catalytic microreactors [15].

Although there exist a wide range of techniques for deposition on structured surfaces [16], only few are compatible with processing on a microscale and give satisfactory results in terms of reproducibility. Due to these limitations, mostly basic techniques such as drop- or spin-coating have been adapted to deposit the catalysts on micro hotplates [17]. These, however, have drawbacks such as poor adhesion and low yield of functioning devices.

Here we propose to use soft-lithographic techniques for deposition and patterning of the boehmite ($\text{AlO}(\text{OH})$) sol used as a support precursor for $\gamma\text{-Al}_2\text{O}_3$.

Soft-lithography is a low-cost technology for the direct deposition and patterning of colloidal suspensions [18]. It was introduced as an alternative technology to standard photolithography allowing microfabrication of high-resolution structures in laboratory conditions [19]. Traditionally, flexible polydimethylsiloxane (PDMS) molds, prepared by casting in a patterned master, are used for transferring the microstructures. The master is prepared by any other lithographic technique which defines the smallest topological feature required. There are several techniques which enable the transfer of a pattern with PDMS molds [20]: microcontact printing (μCP) [21], micromolding in capillaries (MIMIC) [22], microtransfer molding (μTM) and minor modifications of these. The techniques used in this study are schematically demonstrated in figure 1.

In MIMIC, a PDMS mold, containing channels opened from one side, is placed on the surface upside down. When a droplet of the solution to be patterned is applied on one side of the open channels, capillary forces cause spontaneous filling [23]. This technique was successfully applied for the deposition of metal oxides in thick-film gas sensors [24, 25].

In μTM , a material to be patterned is spread over the PDMS mold and placed on the substrate. After temperature-assisted curing, the mold is removed.

Criteria used for the comparison of the selected catalyst deposition techniques are listed as follows:

- (i) feasibility of local deposition;
- (ii) applicability on microscale and compatibility with Si-based sensors and microreactors;
- (iii) smallest possible dimension;
- (iv) simplicity of the method;
- (v) reproducibility of the method;
- (vi) cost efficiency;

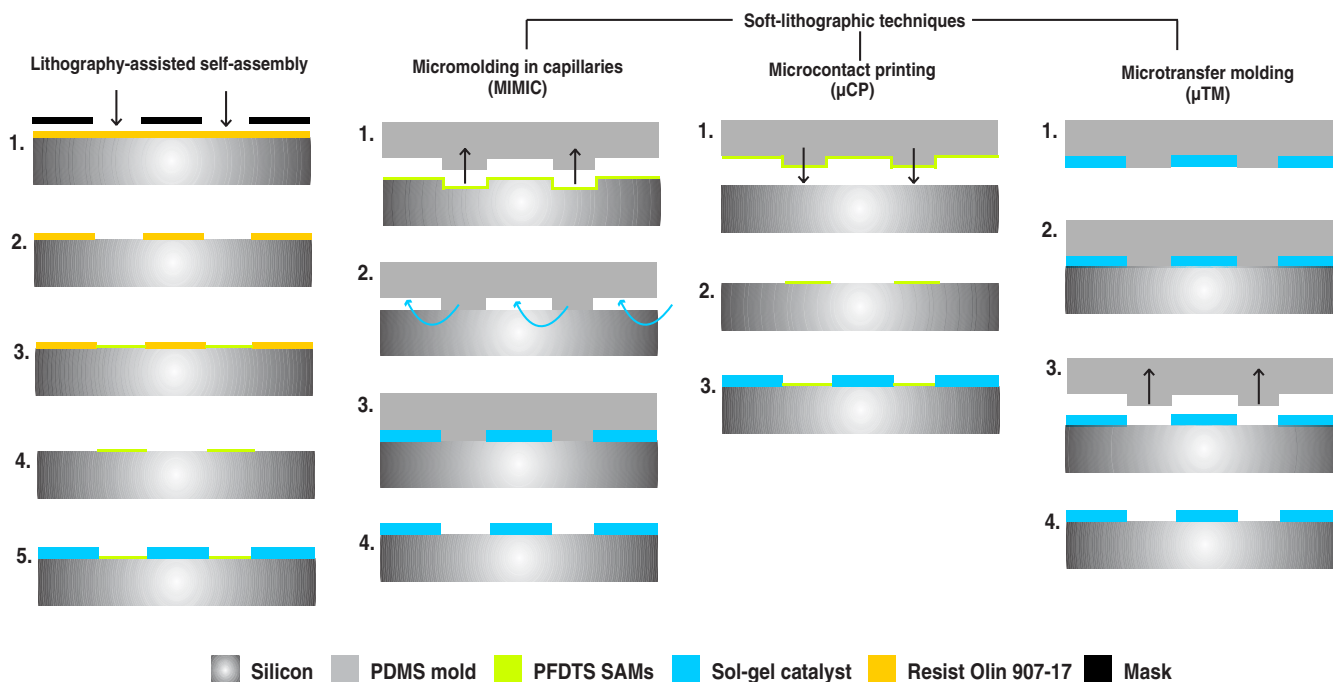


Figure 1. Overview of the techniques used for catalyst deposition and patterning. Lithography-assisted self-assembly of the catalyst: (1–2) pattern definition by UV lithography; (3) CVD of the PFDTS SAM; (4) stripping of the resist and cleaning; (5) dip coating or spinning of the catalyst. Micromolding in capillaries: (1) replica molding of the PDMS mold; (2) conformal contact of the PDMS mold with the Si substrate; (3) catalyst is introduced at one side of the opened channels; filling of the channels due to capillary forces; (4) removal of the PDMS mold. Microcontact printing: (1) conformal contact of the PDMS mold containing the PFDTS ink with the Si substrate; (2) printing of the PFDTS ink and removal of the mold; (3) dip coating or spinning of the catalyst. Microtransfer molding: (1) catalyst deposition on the PDMS mold and removal of the catalyst excess; (2) conformal contact of the PDMS mold containing the catalyst with the Si substrate; (3–4) removal of the mold and release of the pattern.

- (vii) generic deposition approach for various materials;
- (viii) feasibility of wafer scale processing.

In μCP , a PDMS mold is used to transfer a pattern of ‘ink’ to a substrate through conformal contact with the formation of a covalently attached self-assembled monolayer (SAM) [26].

2. Experimental details

2.1. Catalyst preparation

Based on the specifications mentioned in section 1.2, two catalysts were selected as the model system for the catalytic gas sensor: (a) solid thin films of Pt and Pd on Ta and (b) Pt and Pd nanoparticles immobilized on porous $\gamma\text{-Al}_2\text{O}_3$.

2.1.1. Sputtered thin-film catalyst. Pt and Pd thin films with a thickness of 100 nm were deposited at a pressure of 0.066 mbar, in 148 sccm Ar flow, and a power of 200 W using a custom-built DC magnetron sputtering system. Ta was used as an adhesion promoter as it was reported to be stable and resistant in a high-temperature oxidizing environment [27]. Patterning was done using conventional UV lithography and thin-film lift-off (30 min sonication in acetone). Shown in figure 2 is a high-resolution scanning electron microscopy (HRSEM) image of a patterned Pt (100 nm)/Ta (15 nm) thin film formed by a lift-off method. Due to a slight coverage of the resist sidewalls by sputtered metal, so-called ears were formed, visible on the image. The pattern of squares was used

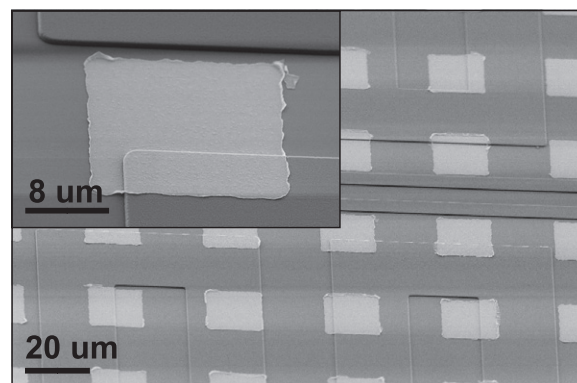


Figure 2. HRSEM image of the Pt/Ta thin-film catalyst sputtered and patterned with the lift-off process on the micro hotplate surface. The magnified image shows the ‘ears’ mentioned in the text, i.e. small protrusions at the edge of the metal pattern.

to distribute the heat homogeneously and reduce the impact of mechanical stress on both the catalyst and catalyst support.

2.1.2. Pt and Pd on sol-gel-based catalyst. Pt and Pd on the γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) catalyst were prepared in four steps:

- (i) the preparation of the boehmite ($\text{AlO}(\text{OH})$) sol, used as a precursor for the $\gamma\text{-Al}_2\text{O}_3$, via the colloidal sol-gel route;
- (ii) impregnation of the boehmite sol with the Pt and Pd precursors;

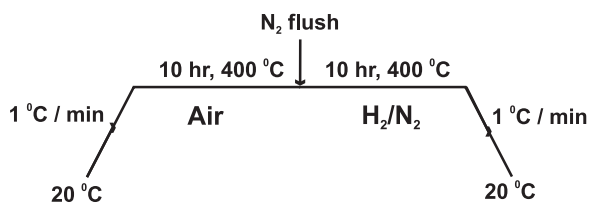


Figure 3. The heat treatment cycle used for the formation of the γ - Al_2O_3 in air and activation of the metal catalyst in H_2/N_2 (10/90 vol. %).

- (iii) calcination in air at 400 °C to form porous γ - Al_2O_3 and decompose the noble metal precursor (PtO , PdO_2);
- (iv) reduction in H_2/N_2 (10/90) at 400 °C to reduce dispersed metal particles (PtO , $\text{PdO}_2 \rightarrow \text{Pt}$, Pd).

The sol-gel method used for the preparation of the boehmite sol was developed earlier [28] and optimized by Biesheuvel *et al* [29] to achieve highly porous, thermally resistant, low-stress γ - Al_2O_3 membranes.

The calcination and reduction temperature profile is shown in figure 3. A temperature of 400 °C and a duration of 10 h were sufficient for the transformation to a stable γ -phase of Al_2O_3 ; additional time (up to 10 h) at 400 °C in the H_2/N_2 environment was given to reduce catalyst particles.

Pt/γ - Al_2O_3 and Pd/γ - Al_2O_3 catalysts were prepared by wet impregnation of the commercial chloride and nitrate precursors. For Pt, the hexachloroplatinic acid solution (H_2PtCl_6 , 20 wt %) and tetraammineplatinum nitrate ($\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, 4 wt %) were used. The precursors used for the preparation of the Pd/γ - Al_2O_3 catalyst were palladium (II) chloride (PdCl_2 , 20 wt %) and palladium (II) nitrate ($\text{Pd}(\text{NO}_3)_2$, wt 14–16 %).

2.2. Soft-lithography

2.2.1. Preparation of the mold. PDMS was prepared by cross-linking of Si-based organic polymer Sylgard 184 (18500 D) with a hydroxy silane cross-linker (684 D) in a 10:1 ratio. The PDMS molds were made by replica molding from a microstructured silicon master, followed by heat treatment at 80 °C for 2 h. The curing rate of the PDMS molds is dependent on temperature. The ratio of polymer to cross-linker and temperature are parameters that influence the mechanical durability of the molds. PDMS affinity toward Si and glass can be modified by treatment in an oxygen plasma. Two types of masters for replica molding were utilized:

- grooves formed by patterning of a layer of the SU-8 resist coated on a Si substrate;
- grooves formed by reactive ion etching (RIE) of a Si substrate through an Olin-1.7 resist mask.

Examples of the masters are shown in figure 4.

2.2.2. Pattern transfer: The following techniques were used for deposition and patterning (see figure 6): direct deposition and patterning of boehmite sol using MIMIC and μTM , chemical patterning (using μCP of functional groups and conventional lithography in combination with chemical vapor

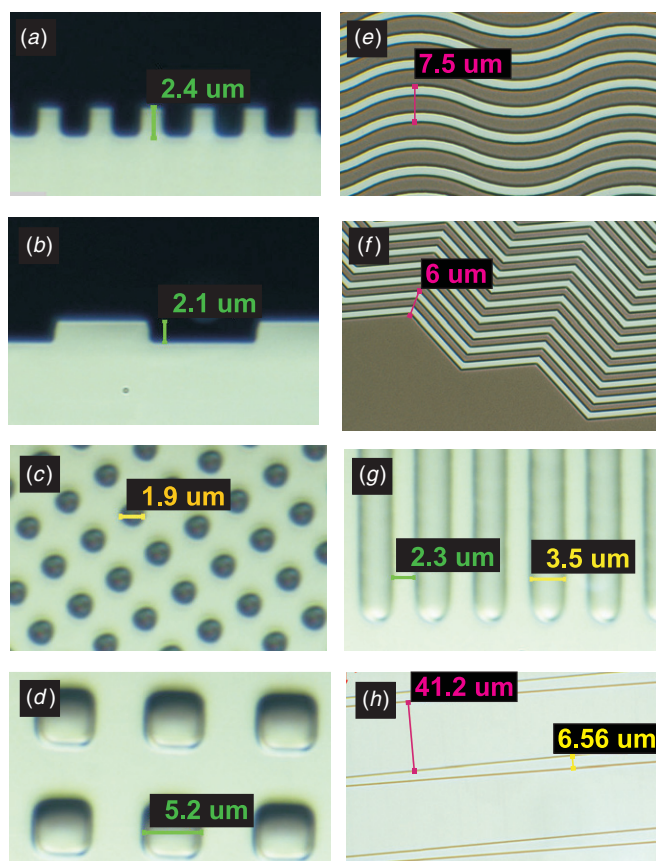


Figure 4. Various designs of the master used as a template for the PDMS mold replication: (a–b) optical imaging of the cross section showing not completely vertical wall profile which corresponds to the effect of underetch from RIE; (c) distortion of the square-shaped pattern due to lithographic limitations; (d–h) stripe and square patterns used as a mask for the surface modification or replicated for direct catalyst patterning with a PDMS mold.

deposition (CVD) of functional groups) with the subsequent deposition of the boehmite sol dropwise using piezoactuated droplet dispensing and using spin- and dip-coating.

The procedure used for patterning using the MIMIC method consists of the following steps:

- (i) the PDMS mold was placed on the substrate ensuring a good conformal contact;
- (ii) the liquid catalyst precursor was placed at the entrance of the open mold pattern;
- (iii) filling of the pattern occurred due to capillary forces;
- (iv) the mold was removed;
- (v) temperature treatment of the patterned catalyst is performed as described in section 2.1.2.

In μTM , the PDMS mold was first immersed in the catalyst solution, followed by the removal of the material excess and then directly transferred onto the substrate. This was followed by curing at ca 100 °C and release of the mold. The curing temperature was selected to be sufficient for evaporation of the water from the catalyst precursor, but below the maximum permitted temperature for PDMS (ca 150 °C).

μCP and lithography-assisted catalyst self-assembly included one more step prior to immobilization of the

catalyst, i.e. chemical surface modification of the oxidized silicon surface using the PFDTS SAMs (1H, 1H, 2H, 2H, perfluorodecyltrichlorosilane).

Oxidized Si is a high-energy solid surface with a high critical surface tension (150 mJ m^{-1}), and therefore wetted by the majority of liquids. The hydrophilicity of the Si surface can be modified with a hydrophobic molecular layer of the type $-(\text{CH}_2)-$ or $-(\text{CF}_2)-$. For hydrogenated and fluorinated coatings, the surface tension drops (20 mJ m^{-1}) and these surfaces exhibit highly non-wetting behavior [30].

To introduce a chemical pattern on a Si surface, we used SAMs of PFDTS. The PFDTS molecule has a fluorinated chain consisting of ten carbon atoms and a silane head-group that binds covalently to a thin layer of native oxide present on the Si wafer. Once oxidized silicon chemically reacts with PFDTS, a fluorinated tail is exposed. The presence of fluorinated groups results in the overall hydrophobic behavior of the self-assembled thin film. The thin films formed are densely packed with a height, measured by AFM, ca 0.8 nm .

The proposed method of pattern transfer is based on CVD of PFDTS [31]. The procedure was developed by Rathgen *et al* [32]. Deposition was carried out in a degassed chamber. The silicon master containing a resist pattern made by UV lithography was exposed to PFDTS vapor. Afterward, the reservoir containing PFDTS was closed and water vapor was introduced to initiate the reaction. By adjusting the pressure, the amount of water and PFDTS vapor entering the chamber can be regulated, thus, leading to the controlled and reproducible deposition of SAMs. The Si wafer contains a layer of resist with defined openings which were exposed to PFDTS. The PFDTS vapor reacts with the oxygen atoms on the Si wafer to form covalent bonds. PFDTS does not react with the photoresist. After the reaction was carried out, the resist was removed in acetone and the wafer was cleaned by immersion in concentrated nitric acid.

3. Results and discussion

3.1. Sputtered thin films

The sputtered thin films have a preferential orientation $\{111\}$ which was reported for identical sputtered thin films by Tiggelaar *et al* [27]. This is an unfavorable orientation when used as a catalyst. It has been reported that the catalyst with densely packed atoms (such as $\{111\}$ or $\{100\}$) exhibits low catalytic activity. Conversely, a catalyst characterized by high-index planes provides more active sites where reactant molecules can interact [33, 37].

The number of active catalyst centers on the surface of the thin platinum catalyst was estimated using chemisorption with 1 % carbon monoxide (CO) 4.7 as a pulsing gas. The experiment confirmed a low surface area of active sites, ca $10^{-4} \text{ m}^2 \text{ g}^{-1}$, see table 1. To increase the accessibility to gas, a square pattern was introduced as described earlier (see section 2.1.1), with the resolution limited by UV lithography to $2 \mu\text{m}$.

The surface area does not change dramatically when patterned. However, the walls and edges of the pattern can be more catalytically active than the top layer. Implementation of

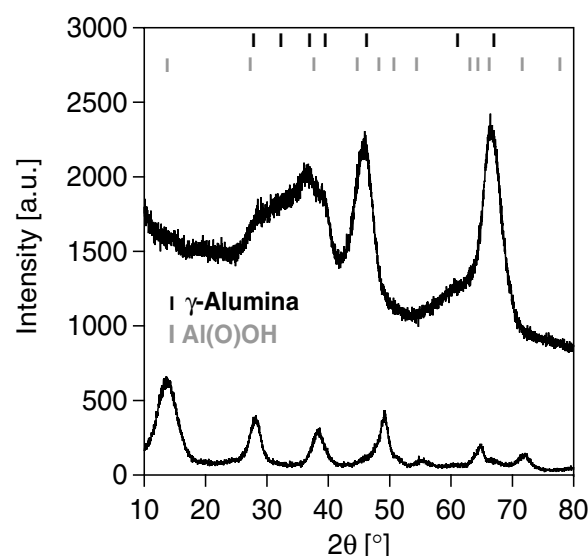


Figure 5. The x-ray diffractograms taken after the preparation of the boehmite sol and calcination resulting in γ -alumina.

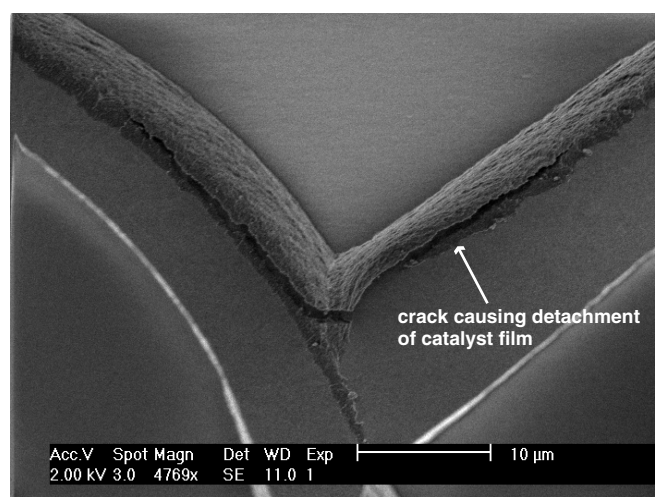


Figure 6. Stress-induced detachment of the catalyst from the substrate.

the pattern results in a discontinuity of the catalyst, i.e. defects acting as reactive centers. An alternative approach would be to roughen the surface of the sputtered thin film, sputter catalytic film on top of another support with higher surface roughness or realize a channel profile in Pt such that the gas can react at both the channel bottom and on the side walls. This would also lead to more efficient storage and distribution of the heat [34].

3.2. Porous thin films

The presence of the desired $\gamma\text{-Al}_2\text{O}_3$ was verified by x-ray diffraction analysis. Shown in figure 5 are the diffractograms taken from the powder samples of uncalcined boehmite sol and γ -alumina. The peaks identified confirmed the formation of γ -alumina. Thermal treatment may cause crack formation and (or) detachment of the catalyst from the substrate (see figure 6). Therefore, 1°C min^{-1} heating and cooling rates

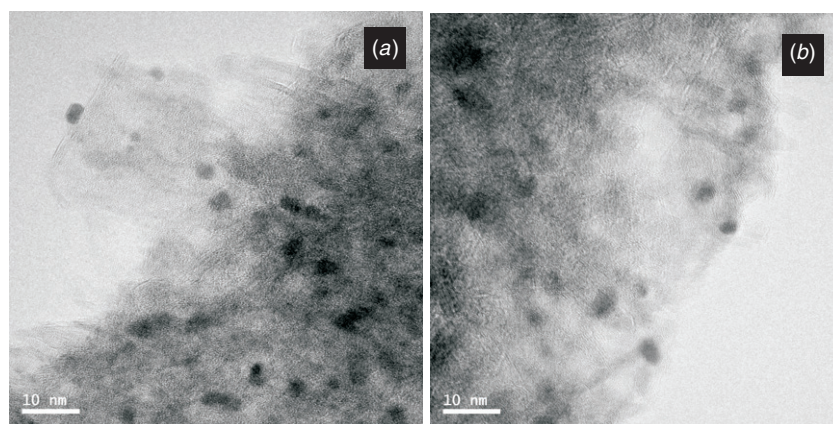


Figure 7. Transmission electron microscopy image of the Pt/ γ -Al₂O₃/5 wt% impregnated from the chloride solution (H₂PtCl₆) (a), Pd/ γ -Al₂O₃/5 wt% impregnated from the nitrate solution (Pd(NO₃)₂) (b) showing well-dispersed catalyst particles with an average size of 5–6 nm.

Table 1. Results of the pulse chemisorption experiments with CO as sorbent gas.

	Composition wt%	Metal dispersion (%)	Metallic surface area (m ² g _{cat} ^a % ⁻¹)	Metallic surface area (m ² g _{Pt} % ⁻¹)	Active particle diameter (nm)
Pt/Ta sputtered	100	– ^b	(1–4) × 10 ⁻⁴	(1–4) × 10 ⁻⁴	– ^c
Pt (nitrate)	5.796	46.2–49.1	6.6–7	114.2–121.3	2.4–2.3
Pt (chloride)	10.41	22.4–25	5.8–6.4	55.4–61.2	4.5
Pd (nitrate)	7.91	12.9–21.9	4.5–7.7	57.7–97.9	5.1–8.6
Pd (chloride)	6.32	32–33.7	9–9.5	142.5–150.5	3.31–3.5

^a By catalyst is meant the sputtered Pt thin film or Pt, Pd on alumina.

^b Could not be identified.

^c Samples with the sputtered thin film were 5 × 20 mm².

were used (to reduce mechanical stresses due to the high temperature).

γ -Al₂O₃ was selected as a support due to the high surface area. The surface area was estimated using the BET method and was found to be 350–400 m² g⁻¹. Pt is well dispersed on γ -Al₂O₃ which can be seen from the transmission electron microscopy analysis (see figure 7) of the powder catalysts prepared. The average particle size is ca 5–6 nm. The smaller the particle size, the larger the amount of low coordinated Pt atoms (defects, edges) that act as reactive centers, thus the higher the activity of the catalyst per gram. Catalysts containing smaller particles are more prone to oxidation and sintering, i.e. faster deactivation, but on the other hand, lead to high metal dispersion [35, 36].

It was found that sols containing a chloride precursor were highly aggressive for the material of the sensor, in particularly to the Al metallization layer. This was attributed to the formation of hydrochloric acid (HCl) during the calcination. Chloride ions, originating from the precursor, were also reported to inhibit catalytic activity [38]. They can be partly removed by high-temperature treatment which is not compatible with the CMOS-based sensor materials. Impregnation of boehmite sol with platinum nitrate is preferred due to a low pH of the resulting catalyst solution.

Pulsed CO chemisorption was used for the determination of the active Pt and Pd surface, the size of the active catalyst particle and metal dispersion. The results of chemisorption experiments are given in table 1. The metallic surface area is several orders of magnitude higher for the porous catalysts compared to the thin sputtered catalyst.

3.3. Choice of the catalyst

The surface area, dispersion and activity of a metal phase are interrelated parameters which dictate the choice of catalyst.

Sputtered thin films are characterized by a low surface area and, if there is a non-active phase present on the top layer, low activity. However, introducing a pattern may resolve this issue. The catalyst does not require any specific activation procedure after deposition and can be used directly.

Sol-gel-based supports ensure a high surface area and a high dispersion, resulting in high activity. However, a procedure for the selection of a suitable catalyst precursor and activation procedure is required. Moreover, the catalyst cannot be used subsequently and needs to be activated.

3.4. Deposition on chemically patterned Si

The surface of oxidized silicon was chemically modified using the PFDTS SAMs as discussed in section 2.2.2. The motivation for this is to introduce areas with different surface energies, i.e. with hydrophobic or hydrophilic (non-wetting or wetting) behavior. When applied on top of such surface, the catalyst ‘feels’ the pattern and shows a different affinity toward patterned and non-patterned surfaces: repelled from the hydrophobic areas and adhering on hydrophilic sections. As a result, deposition can be achieved selectively and locally: on the area of interest. This technique allows the controlled deposition and patterning of the catalyst in a non-destructive manner, for both the sensor and the catalyst, with a resolution limited only by the mask fabrication method. The wetting

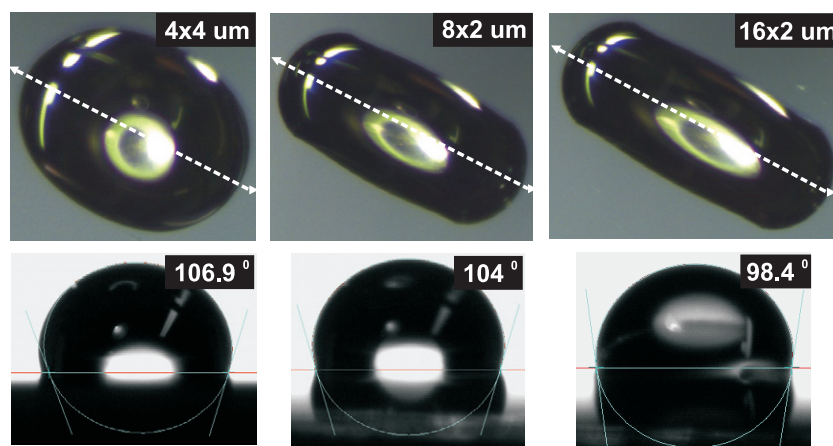


Figure 8. Droplets of the boehmite sol deposited on the chemically patterned surface (the white line shows the direction of the line pattern) with various ratios of hydrophilic and hydrophobic areas; corresponding contact angles are shown below each photograph.

behavior of the boehmite sol on a patterned Si surface was investigated. Boehmite sol, used as a precursor for γ - Al_2O_3 , has viscosity and wettability properties close to those of pure water. The viscosity of boehmite was measured at room temperature and found to be equal to ca 3.5 mPa·s (for comparison, the viscosity of water is 1.002 mPa·s). This is an important property for the material to be patterned by various soft-lithographic techniques. The boehmite droplets (the volume of dispensed droplets kept constantly 3 μl) deposited on the stripe-patterned surfaces are demonstrated in figure 8. The stripe pattern was realized with various widths of hydrophobic and hydrophilic areas. Symmetrical patterns, such as $4 \times 4 \mu\text{m}$, result in a (nearly) round shape of the boehmite droplets.

When the width of the hydrophilic part was increased compared to chemically modified hydrophobic areas, such as from 8×2 to $16 \times 2 \mu\text{m}$, elongation of the droplets was observed. Similar behavior was observed with water and glycerol with a mechanism for this explained in [39, 40].

The difference in the affinity of the boehmite sol to hydrophobic and hydrophilic areas causes a deformation of the droplet and preferential orientation along the lines. Thus, by creating a specific pattern, manipulation with a limited amount of the catalyst precursor is possible. When the volume deposited becomes too large, the macroscopic effects play a more important role and the boehmite sol does not respond anymore to the hydrophobic/hydrophilic pattern underneath the droplet volume. Contact angle measurements of boehmite and water droplets on equally patterned surfaces indicated nearly the same angles (ca 100°), from which we can conclude that the wetting behavior of boehmite is similar to that of water. Spin coating and dip coating can be used to deposit the boehmite on a chemically patterned surface. Figures 9 and 10 show the examples of the self-assembled boehmite for wide lines and squares.

It was possible to achieve stable adhesion of the catalyst, which was tested by sonification in water. After 20 min of ultrasound treatment, no mass loss was observed.

The formation of the PFDTs SAM chemical pattern on Si can also be achieved by the μCP method. Although it was reported as being successfully applied in patterning of colloidal

suspensions [41], in our case this method is less promising. Silanes are known for being unreactive when an insufficient amount of water is present. On the other hand, in an excess of water they tend to polymerize. Therefore, deposition has to be carried out in a controlled environment, e.g. a glove box, and even then humidity control is crucial. The polymerization reaction requires a defined amount of time; thus when directly exposed to air, the printed ink still keeps its properties for a few minutes, but this reduces the reproducibility of the patterned films. Moreover, the μCP technique in most of the cases requires the transfer of the pattern chip by chip. Therefore, the procedure of surface modification by μCP alone is a time-inefficient process with a low rate of success.

3.5. Direct deposition using the PDMS mold

The MIMIC technique was utilized for patterning of boehmite sol on microstructured surfaces. In figure 11, an example of the pattern achieved by MIMIC is demonstrated. Structures with a resolution down to 4 μm were achieved. This method can be adopted for the patterning of various liquid catalyst precursors. However, in each case an experimental procedure needs to be developed at which the affinity of the material to be patterned is higher toward the solid surface than the mold, to prevent sticking.

Additionally, after calcination, the γ - Al_2O_3 tends to shrink, causing the deformation of the original pattern. This factor has to be considered in the original design.

In μTM , the catalytic precursor is transferred by the mold. After placing the mold containing the precursor on the substrate, a temperature treatment is applied to dry the catalytic precursor. The main factor limiting the implementation of this technique is the time for adjusting the affinity of the material to the mold and substrate in combination with the temperature treatment step. These factors cause sticking of the catalytic material to walls of the PDMS molds. In addition, the initial removal of the catalyst excess results in non-clean conformal contact with the substrate. For these reasons, the method is regarded as less efficient for the purpose of the sol-gel catalyst deposition.

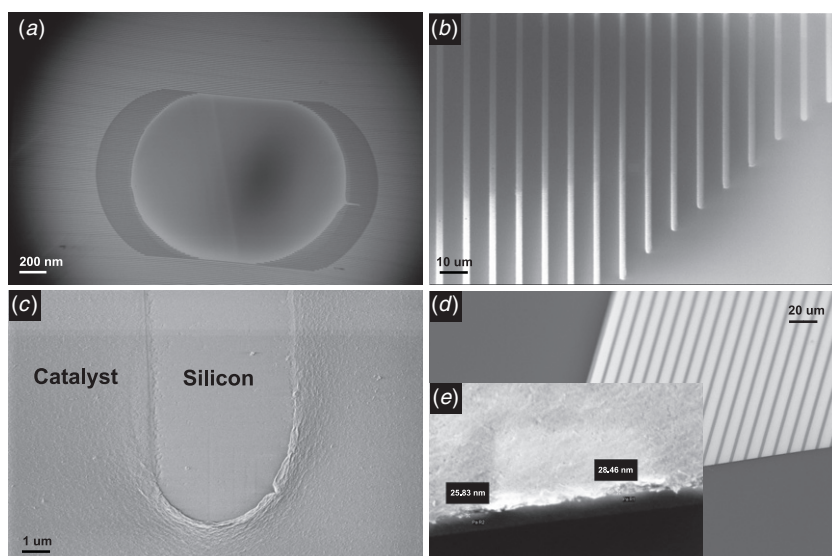


Figure 9. HRSEM images of the boehmite patterns obtained by droplet-wise deposition (a), pinning effect at the edges of the deposited droplet (b), self-assembly of the boehmite on a non-patterned silicon surface and free of catalyst chemically modified surface (c), and cross-sectional view of patterned structures (d) showing average thickness in the order of 25–30 nm (e).

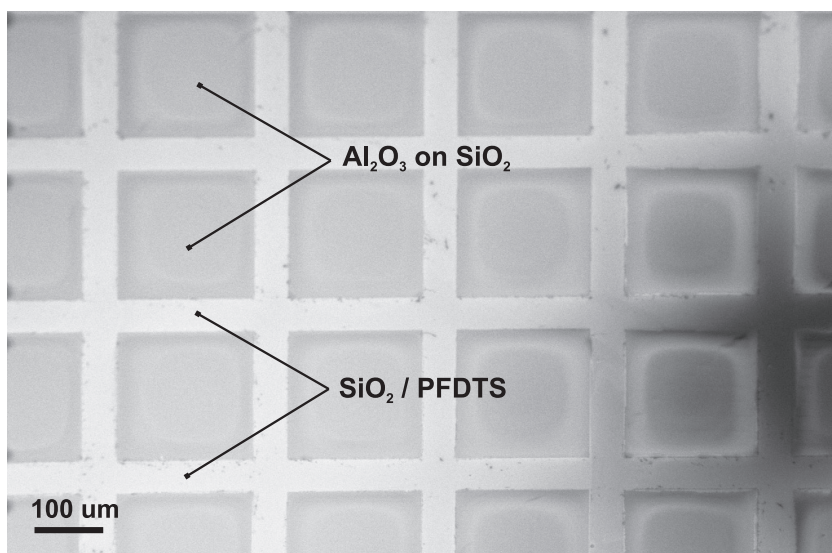


Figure 10. Square pattern of the catalyst thin film obtained by dip coating of the chemically patterned Si/SiO₂ substrate in the boehmite solution. Low-energy (hydrophobic) areas with immobilized PFDTs SAM repel the boehmite, and the high-energy (hydrophilic) SiO₂ surface facilitates the deposition of the boehmite.

3.6. Choice of the deposition technique

In this study, we aimed at selecting a technique which can be directly applied for the deposition of sol–gel-based catalysts, which does not require a long tuning procedure for the material to be patterned and gives reproducible results.

The best results in terms of reproducibility and time efficiency were achieved by lithography-assisted self-assembly of the catalyst sol and the MIMIC techniques.

Among the advantages of these methods are the following:

- (i) non-destructive method for both the patterned catalyst and the substrate;
- (ii) low cost;
- (iii) can be adopted fast to different types of catalyst precursors;

- (iv) the procedure itself is not time consuming;
- (v) provides the possibility for wafer scale deposition.

The minimum achievable dimension is limited by the mask fabrication process and wetting properties of the immobilized catalyst precursors.

By wafer scale deposition, we mean the following (see figure 12):

- the deposition of various catalyst precursors using a single PDMS mold;
- the deposition of one catalyst precursor from the mold replicated from a wafer and placed on a rigid support to ensure mechanical stability.

An example of a machine facilitating wafer scale printing of a catalyst can be found in the literature [20].

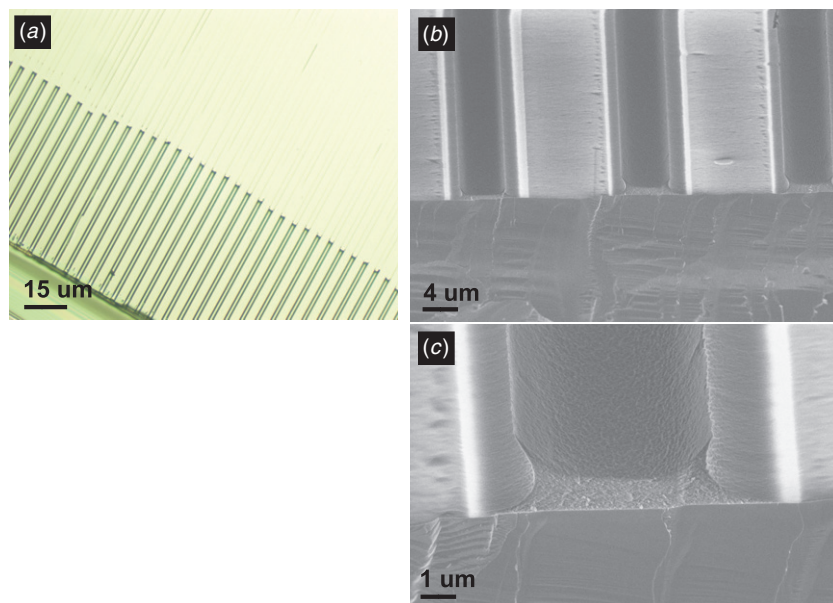


Figure 11. Instantaneous filling of the PDMS channels due to capillary forces (a), the $\gamma\text{-Al}_2\text{O}_3$ pattern obtained by the MIMIC technique (b) and close up showing sintering of the oxide during the calcination (c).

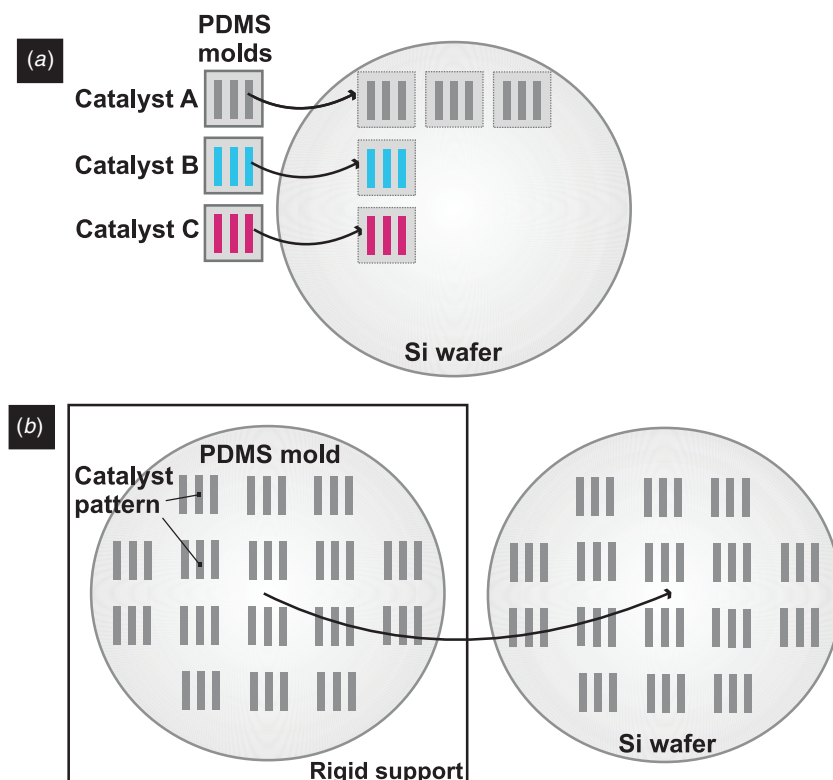


Figure 12. Upscaling of soft-lithographic techniques to wafer level.

4. Summary and conclusion

Sputtered thin films and the sol–gel-based catalyst were investigated as functional coatings in catalytic microsystems.

Sputtered thin films can be deposited and patterned in a straightforward way using magnetron sputtering in combination with standard photolithography, metal lift-off or wet etching. The catalyst does not require any specific

activation procedure and can be used directly. These thin films, however, are characterized by a low surface area and, if there is a non-active phase present on the top layer, a low activity. Such a low activity of the catalytic film, however, may not be an issue when implemented for highly active chemical reactions. Additionally, a micro- or nanopattern can be introduced to increase locally the surface area. High temperatures should be avoided as they cause sintering and lead to the decrease of the active surface area.

Sol-gel-based supports ensure a high surface area and a high dispersion of active metal phase, resulting in high activity. Sol-gel-based catalyst precursors require the development of specific deposition and patterning techniques and high-temperature activation procedures (calcination, reduction). In these thin films, loss of activity at high temperatures due to the sintering of metal particles is significantly less compared to the sputtered thin films. Soft-lithographic techniques were applied for the deposition of a boehmite sol. In terms of reproducibility, lithography-assisted self-assembly and MIMIC are considered as the most promising techniques to pattern a sol-gel-based catalyst.

Both the sputtered metal and the metal dispersed sol-gel-based γ -alumina thin films were characterized and exhibited catalytic activity. Thin sputtered films are less active compared to sol-gel-based catalysts due to the low surface area. However, this can be sufficient when implemented in highly reactive systems or if sensitive measurement methods are applied [3].

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