

Full Paper

Wet Chemical Synthesis and Screening of Thick Porous Oxide Films for Resistive Gas Sensing Applications

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Abstract: A method of wet chemical synthesis suitable for high throughput and combinatorial applications has been developed for the synthesis of porous resistive thick-film gas sensors. This method is based on the robot-controlled application of unstable metal oxide suspensions on an array of 64 inter-digital electrodes positioned on an Al₂O₃ substrate. SnO₂, WO₃, ZrO₂, TiO₂, CeO₂, In₂O₃ and Bi₂O₃ were chosen as base oxides, and were optimised by doping or mixed oxide formation. The parallel synthesis of mixed oxide sensors is illustrated by representative examples. The electrical characteristics and the sensor performance of the films were measured by high-throughput impedance spectroscopy while supplying various test gases (H₂, CO, NO, NO₂, propene). Data collection, data mining techniques applied and the best potential sensor materials discovered are presented.

Keywords: Combinatorial Chemistry, High Throughput, Thick Film, Sol-Gel, Sensor, Materials Science.

1. Introduction

The industrial and private sectors provide a growing market for new sensor materials due to the variety of old and new application areas. However, the quality characteristics of good sensors for the gas analysis - above all rapid response behaviour, high selectivity and stability - need development

periods that are currently limited by their large demand in time and manpower. This is a direct consequence of the methods used in this field, dominated by empirical optimization of known sensor materials with the help of the synthesis parameters within the manufacturing process. Additional problems are the difficult physico-chemical relationships of the interaction of complex structured sensitive solids with the vapour phase, which has not yet been completely understood [1]. Here, high-throughput (HT) methods allow to create more efficient processes for the development of new gas sensors by introducing parallelization and miniaturization into the development processes, thus minimizing time and effort. Polymeric sensor materials bring a high diversity for the detection of chemical and biological agents in gases and liquids. Sensing concepts cover ion-selective electrodes, optochemical sensors, composite resistor polymeric films for vapours, conducting polymer biosensors, and polymeric biosensors. A typical example is the use of an 8 x 12 micro-array to deposit polymers by electrochemical synthesis, followed by HT characterization of response time, recovery time, reversibility, reproducibility, sensitivity and linearity [2]. Optical sensor materials are responding to analytes with a change in optical properties, such as absorption, reflectivity, luminescence or optical decay. A typical example of HT development of such sensors is provided by Apostolidis *et al.*, who describe the automated selection of most suitable combinations of polymers types and indicators with plasticizers for O₂-detection [3]. The combination of HTE with microfluidics and micro- and nanofabrication and has been leading to innovative sensor solutions. The field of polymeric sensor materials has been reviewed recently by R. Potyrailo [4].

Several HTT have been developed, which allow extensive parameter screening for various types of sensor materials. The use of vapor deposition to prepare electrode arrays on Si wafer [5], is limited, since porosity, composition and microstructure, which affect sensing properties, cannot be controlled properly. Wet synthesis of mixed oxides was combined with a ceramic library on an Al₂O₃ library plate with 64 printed Pt electrodes for development of resistive sensors [6]. Sol-gel synthesis could be applied by the use of a special reactor, which allowed parallel measurement of temperature effects and resistance during exposure to pollutants [7]. Completely automated determination of sensoric responses with HT impedance spectroscopy (in the frequency range of 10 up to 10⁷ Hz) has also been reported [8]. The complete set up for HT impedance screening for gas sensing materials has been described [7] with doped In oxides as potential sensor materials for hydrogen. A workflow and HT analysis with impressive visualization for screening of sensor properties applying a sequence of pollutants has also been reported [9]. HT-screening with gas sensor systems has also been explored in various applications by the group of Y. Yamada. They have combined gas sensing semiconductors for the rapid analysis of benzene derivatives in HTE [10].

In this work the use of HT-methods for the study of resistive gas sensors based on selected metal oxides should provide access to novel suitable materials. The advantage of the use of HT-methods compared to conventional methods here is, that 64 samples can be studied in parallel und the sensing conditions for all samples are identical, so the data are comparable. Furthermore, the samples are prepared with the help of pipetting robots, so the reproducibility is high and rapid. Microstructural differences are avoided by using the identical procedure for all syntheses and film preparations. Furthermore, by using complex impedance spectroscopy as characterization tool it is not only possible to evaluate the sensor properties of the materials, but also to gain access to information on physical or surface-specific parameters such as the conductivity at grain boundaries or the mechanism of electrical

conduction within the sensor is obtained [11]. With reference to the sensor morphology it has to be differentiated between compact thin films, where an interaction with the gas only takes place at the geometric surface, and porous layers, where the whole volume provides active surface.

The semi-conductive properties of metal oxides represent the basis for their use as resistive gas sensors, since the number of free charge carriers within the metal oxide and thus its electrical conductivity reversibly depends on the interactions with the ambient gas atmosphere. In classical sensor materials charge transfer either results from adsorption or chemisorption of gas molecules at the sensor surface (e.g. SnO₂), or from diffusion of the gas into the bulk of the sensor material (e.g. TiO₂) [12]. Fine-tuning of the sensor selectivity can be achieved e.g. by varying either the crystal structure/morphology, doping, or operating temperature. The necessary operating temperature of the sensor during application is adjusted by heating with a platinum wire, located within the material via an energy supply of approx. 1 Watt. Some examples of literature known resistive sensors materials for nitrogen oxides and hydrocarbons are given in table 1. The comparison of the limits of detection (LOD, defined as $R_{\text{gas}} / (R_{\text{reference}} \cdot c_{\text{gas}})$ [1/ppm]) of these sensors at the optimal response temperature makes only sense regarding comparable concentrations of model gases. It originates in the nonlinear responding behaviour of sensors in general which results in a decrease of the relative change in the sensitivity at high gas contents.

Table 1. Figures of merits of comparable sensors for nitrogen oxides and short-chained hydrocarbons.

materials used	test gas	response temperature	c(gas) [ppm]/ LOD [1/ppm]	cross sensitivity against	ref.
0.5 at% Ba/ In ₂ O ₃	NO, NO ₂	300°C	10/~1 3/~4	octane	13
Pt/NaZSM5	C ₃ H ₈		500/~6·10 ⁻³	-	14
Pt/SnO ₂	NO, NO ₂	room temperature	20/~0.83 30/~0.24	-	15
SrTi _{0.6} Fe _{0.4} O ₃	C ₃ H ₈	400°C	3000/~9.2·10 ⁻⁴	-	16
SnO ₂	C ₃ H ₈	250°C	400/~0.14	CH ₄ , toluene	17
Al, Ni/SnO ₂	LPG	300°C	600/~0.16	-	18
Pd, Sb, In/ SnO ₂	C ₃ H ₈	500°C	500/~0.04	C ₂ H ₅ OH	19
BaTiO ₃	C ₂ H ₄	500°C	700/~2.3·10 ⁻³	O ₂ , NH ₃	20

LPG = Liquefied Petroleum Gas

Unlike other classes of materials, mixed metal oxides offer the advantage of comparably simple production and broad availability, and at the same time provide the potential for a sufficiently low base resistance and an adequate durability in long-term operation. Their use is currently still restricted by the cross sensitivity of the known sensor materials.

Lately mixed metal oxides, which combine the positive sensor properties of the pure components, are used for gas detection purposes [12, ¹³, ¹⁴]. However, with the help of classical synthesis methods of oxidic sensors such as sputtering, CVD (chemical vapour deposition), PLD (pulsed laser deposition), and MBE (molecular beam epitaxy) [15, 16, 17] only thin films can be produced. It is often not possible to retain the properties of thin films while transforming them into bulk materials of porous powders, often used as sensor materials in industries. Thus, in order to enable combinatorial synthesis and measurement of bulk resistive gas sensors, this work is based on the production of thick porous metal oxide films. An additional advantage of thick porous films is the large specific surface areas as well as the long residence time of the gas species, which results from diffusion into the material.

In general, the screen print process is a widespread method to produce 1 to 300 μm thick films in research and development. Relative to the classical methods, such as impregnation and co-precipitation, the sol-gel technology offers several advantages for the production of mixed oxides, since it allows broad variations in precursors and directed introduction of doping elements. Furthermore, the sensor morphology can be well tuned by the adjustment of synthesis parameters, the drying period, calcination times and temperatures. Up-scaling and transformation into pastes of optimised sol-gel-based porous powders can be more easily handled than materials, created with the help of other preparation methods. The combinatorial synthesis of mixed-oxide inorganic materials is common practice. [18, 19]. However, in order to produce inorganic films of μm thickness additional factors have to be considered. The homogeneous film-formation by direct application of a sol onto a support medium is affected by the gel-forming process. On the one hand, cracks and poor adhesion of the films can result from syneresis through aging of the gel films or by rupturing of the films caused by the strong capillary forces during gel drying. On the other hand, due to edge effects, which dominate the coatings of small areas, the critical film thickness is often exceeded at the sensor edge, which cause the films to blister. To avoid these effects a complex process optimisation has to be carried through for each individual metal oxide system, e.g. by introducing additives without success guaranty. Weller for example produced perovskite-films in parallel at temperatures of up to 1200 C° by direct formation of oxide sols on the substrate, where problems such as crack-formation, inhomogeneous film-forming, and soaking of solutions through the mask could not be avoided [20]. This work describes the development of an alternative preparation method, which does not rely on direct sol application, but uses instead unstable suspensions of pre-manufactured metal oxides as starting materials for the combinatorial thick film preparation. A similar procedure has already been used for manual production of TiO₂ thick-films on Al₂O₃ by Savage [21]. Sterzel and Kuehling [22] have patented a procedure based on the application of suspensions, stabilized by dispersing agents. Gao has used inkjet printing of metal oxide suspensions to combinatorially produce thick films of rare-earths metal oxides [23]. In this study, the suspensions are stabilized by time-consuming milling of oxide powders mixed with water.

The goal of our investigations focuses on the development of a methodology for an high throughput synthesis of thick film sensors as well as a screening tool for sensor testing to discover new selective material classes. Important sensor parameters like film thickness, porosity, microstructure, phase purity or sintering temperature cannot be investigated in detail in this combinatorial workflow. These properties should be analyzed and improved in a subsequent conventional optimization step with

selected new materials. For the combinatorial sensor synthesis of this work SnO₂, WO₃, ZrO₂, and TiO₂, the classical sensor materials, were chosen as base oxides as well as the oxides CeO₂, In₂O₃, and Bi₂O₃. CeO₂ is an n-doped semi-conductor and a potential sensor material with a good stability against corrosive and reductive gases [24]. Due to the large number of oxygen defects in the lattice, In₂O₃, which is also an n-type semiconductor, is well known to possess a high electrical conductivity and to be a sensorically active material, especially in combination with tin oxide (ITO) [25]. Bismuth oxide films show remarkable catalytic properties in oxidation reactions due to the high oxygen ion mobility at the film surface, and, thus, are highly interesting for the development of sensors [26]. A new and easy strategy for the combinatorial synthesis of thick film sensors using this metal oxides is revealed. After exposing suitable sensor libraries containing doped base oxides with the selected set of test gases in synthetic air (H₂, CO, NO, NO₂, propene) the materials are evaluated regarding their sensor properties and inter-sensitivities with the help of the complex high-throughput impedance spectroscopy (HT-IS). Basic requirement for the HT-IS measurements is a sufficient electric conductivity of the semiconductor base oxides which depends on their different band gaps. It was also examined whether the parameter selectivity and electric conductivity of the sensor could be improved by forming mixed oxides of selected materials. This report will exemplarily present some trends and results of these investigations. This is a high throughput investigation with emphasis on screening and function. It does not provide optimal materials, but the relative behaviour of potential sensor materials under comparable sensing conditions. To turn these materials into useful sensors would require optimisation of the solid state synthesis, materials characterization and conventional testing.

2. Experimental

The application of the thick film sensors was carried out on an aluminium oxide support of a lateral size of 110 x 110 mm², which is structured by 64 inter-digital capacitors made of Pt and which allows to parallelly produce 8x8 coatings [27]. By means of the synthesis robot (Packard Multiprobe II EX) the prefabricated suspensions were introduced into a synthesis reactor that allows a suspension application of a maximum of approx. 120 µl over a mask into a cavity above the sample spot (diameter of 4 mm) [8]. To guarantee their utmost homogeneity the mixed-oxide powders were milled in a ball mill, and, afterwards, the larger particle aggregates were separated by wet filtration with the help of an analysis sieve (10 µm pore size), in order to prevent the pipetting tip of the synthesis robot to be clogged. A suspension of the sieve fraction was prepared using a suitable alcohol (concentration: 20 through 40 mg/ml), and was stirred with approx. 1000 rpm during the sensor formation. For this purpose, a magnetic stirrer or a multiple magnetic stirrer plate were used by the robot during slurry preparation. The doping agents were already introduced during the preparation of the slurry.

The base oxides and the suspensions (slurries) were prepared according to the following recipes:

SnO₂: 2.40 ml acetylacetone in 4.00 ml THF are added to a solution of 3.03 g Sn(IV)isopropoxid (98%, Alfa Aesar) in 7.09 ml THF. 200 µl 1M HNO₃ in 4.00 ml THF are added dropwise. After 5 min. 200 µl 1 M HNO₃ are added. The resulting gel is dried at 100 °C and milled in an agate mortar. The resulting powder is calcined for 6 h at 400 °C (heating rate: 100 °C/h). The slurry is prepared from a mixture of 10 ml polyethylene glycol 600 (purum, Roth; 5 wt% in isopropanol), 116 mg SnO₂ in 4 ml isopropanol, and, if necessary, 2 ml of the dopant solution in isopropanol.

WO₃: 584.1 µl HNO₃ (65%), and, if necessary, 0.25 molar aqueous doping salt solutions are added to a solution of 8.18 g ammonium (meta)tungstate hydrate (purum, Fluka) in 30 ml water. The sol is dried at a temperature of 80 °C, milled and calcined for 6 h at 500 °C (heating rate 100 °C/h). The slurry is prepared from the powder and isopropanol with a ratio of 30 mg : 1 ml.

ZrO₂: 200 µl HNO₃(65%) is added to a solution of 2.00 g zirconium(IV)-propoxid (70%, ABCR) in 2.00 ml THF and stirred for 90 min. The hydrolysis is carried out after adding 100 µl water in 6.5 ml THF. The sol is dried at 40 °C until it forms a transparent gel, which is milled and dried again, first for 2 h at 60 °C and then for 2 h at 80 °C. The calcination is carried out for 6 h at 500 °C (heating rate 100 °C/h). The slurry is prepared from 191 mg powder in 8 ml isopropanol, and, if necessary, 2 ml of the dopant solution in isopropanol. In order to improve the adhesion properties on the substrate a mediating sol, consisting of 2.88 g zirconium(IV)propoxid (70%), 0.45 ml ethyl acetoacetate, and 3.94 ml isopropanol is added.

Bi₂O₃: 1.00 g HNO₃ (65%), and 295 mg polyvinyl alcohol Mowiol 18-88 (Clariant, 10% in H₂O) are added to a solution of 1.00 g Bi(NO₃)₃*5 H₂O (>99%, Fluka). The sol is dried at 90 °C until a transparent glass is formed, which is milled and calcined for 6 h at 500 °C (heating rate 100 °C/h). The slurry is prepared from 168 mg powder in 5 ml 1-propanol, and, if necessary, 2 ml of doping solution in 1-propanol. The mediating sol is made by mixing 147 mg Bi(III)-2-ethyl-hexanoat (Alfa Aesar), 8.00 g 1-Propanol, and 23 mg acetylacetone and added to the slurry.

TiO₂: 15.2 g Ti(IV)isopropoxid (97%, Aldrich) is added dropwise to 24.3 g 1-propanol and 1.12 g HNO₃ (65%). After stirring for 30 min 3.00 g water are added dropwise for hydrolysis. The gel is dried at 90 °C. Calcination is carried out for 6 h at 700 °C (heating rate of 100 °C/h). The slurry is prepared from 179 mg oxide in 10 ml isopropanol, and 0.62 g of the mediating sol in 9.38 ml 1-Propanol. The mediating sol consists of 1.90 g Ti(IV)isopropoxid, 1.34 g acetylacetone, 0.14 g HNO₃ (65%), 0.188 g water, and 2.42 g 1-propanol.

CeO₂: 0.259 g HNO₃ (65%), and 1.93 g polyvinyl alcohol Mowiol 18-88 (Clariant, 10 wt% in H₂O) are added to 5.75 g cerium nitrate (99+%, Fluka) in 47.5 g water. The sol is dried at 90 °C. Calcination is carried out for 6 h at 700 °C (100 °C/h heating rate). The slurry is prepared from 298 mg oxide in 10 ml ethanol. The mediating sol consists of 0.58 g cerium nitrate, 144 mg polyethylene glycol 600 (10 wt% in ethanol), 26 µl HNO₃ (65%), and 5.65 ml ethanol.

In₂O₃: 2.00 g indium nitrate (99.99%, Aldrich) is mixed with 10 ml propionic acid and heated to 140 °C until the formation of nitrous oxides is completed (fill up again with propionic acid may become necessary). The transparent glass is milled and is calcined for 6 h at 500 °C (heating rate of 20 °C/h). The suspension consists of 150 mg oxide powder and 5 ml 1-propanol.

In₂O₃/WO₃ mixed oxide library: Adaption of the In₂O₃-recipe to the water-based WO₃ oxide recipe. 0.367 g polyvinyl alcohol Mowiol 18-88 (Clariant, 10% in water), and 37 µl HNO₃ (65%) are added to 1.74 g In(NO₃)₃*5 H₂O in 6.77 ml water, and are stirred. An equimolar WO₃ solution is made according to the above recipe. A composition spread is created using an increment of 10 at% under addition of a 0.02 molar solution of the bulk doping agent in water. 1.5 ml of the mixed oxide soles are pipetted into Eppendorf vials, shaken, dried at 70 °C and are calcined in GC vials for 6 h at 500 °C. The suspensions consist of 18 mg mixed-oxide powder in each case and 1.2 ml isopropyl alcohol.

In order to prepare the material libraries with one main component the oxides were suspended into glasses with a lid, and were stirred at 1000 rpm during pipetting by the synthesis robot. To prepare the

mixed-oxide sensors the suspensions were filled into GC vials, simultaneously stirred by a multiple magnetic stirrer, and were pipetted one after the other. As to the synthesis of the In/W mixed-oxide library, both base oxides were made by using one common recipe. The pipetting volume of the suspensions was adjusted to a quantity of oxide per sample spot on the aluminium oxide support, which corresponds to a nominal film thickness (relating to dense oxide) of the sensors of approx. 10 μm . The actual film thickness will be considerably larger due to the fact that a porous film will be formed. Surface dopings can be applied by primarily introducing suitable solutions of the selected precursor of the doping element.

After deposition of the suspensions by the robot the solvent is evaporated at ambient temperature, the sample plate is removed from the synthesis reactor, and is calcined (heat to 180 °C with 1°C/min, maintain for 1 h, heat to 450 °C, maintain for 1 h, heat to 700°C (500°C for In_2O_3), maintain for 1 h, cool down). After supplying the gases the regeneration of the sensors is carried out by calcination for 1 h in ambient air at a temperature of 700 °C.

The high-throughput impedance spectroscopy is carried out with a set-up described by Simon and coworkers [27]. In order to save the synthesis and measurement data as well as to evaluate the data a project-oriented database (MS Access™) was used [28]. The composition of the mixed-oxide library samples was studied by X-ray fluorescence spectroscopy with the system EAGLE μ -PROBE II (Röntgenanalytik Messtechnik) with the help of an x-y-z-table. The XRD measurements were carried out with a diffractometer (Siemens D5000) equipped with Bragg-Brentano-type path of rays and a 1-mm-collimator aperture stop.

With respect to the impedance spectroscopy (IS) measurements 4 target temperatures (400, 350, 300, and 250°C) were fixed in order to test the sensors, and were activated ranging from the highest to the lowest temperature. Within the measurement procedure the test gases that are primarily mixed with synthetic air are introduced sequentially with pure synthetic air, which serves as a reference gas. The gas supply of the sensor libraries is carried out for 15 min for each gas according to the following listing: air, H_2 (50 ppm), air, CO (50 ppm), air, NO (5 ppm), air, NO_2 (5 ppm), air, and propene (50 ppm), air. Here, the reversibility of the sensor performance is evaluated by supplying synthetic air after each supply of test gas.

3. Results

3.1. Sensormaterials based on single oxides

The method of applying metal oxide suspensions compared with the sol-gel method of direct coating offers the advantage of a controlled synthesis of the base oxides prior to the actual coating, which enables a more defined introduction of bulk and surface doping. Here, bulk doping means that the doping element is homogeneously distributed in the bulk of the matrix oxide. Furthermore, it is advantageous to separate oxide synthesis and film application in order to maintain a higher variability in the automated workflow. The doped metal oxide powder is prepared from the element precursors, acid, solvent, and the especially for the system optimised additives (complexing agents, organic binding agents, doping substance) as shown in fig. 1.

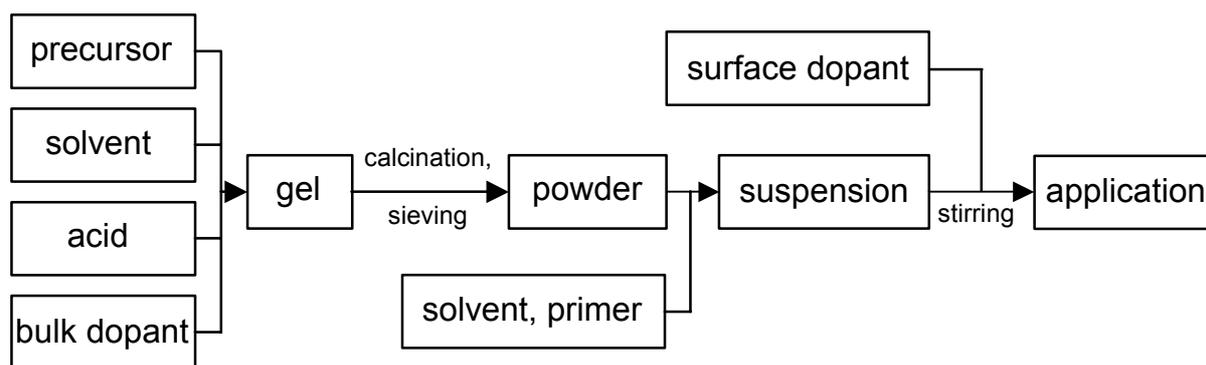


Figure 1. Workflow for the coating of suspensions.

For coating additional adhesive agents (bonding agents or oxide soles) and a surface doping agent may have to be added. In addition to introducing the adhesive agent the adhesion on the Al_2O_3 support is also improved by sintering the particles during the thermal post-treatment at 700 °C. Fig. 2 shows the temporal course of film forming during the robot-controlled pipetting procedure. The solution containing the surface doping and the adhesive agent is pipetted into the cavity of the mask over a sample spot in the synthesis reactor, positioned above one of the 64 inter-digital capacitors of the substrate (a). The slurries or suspensions are added at the end for even sedimentation on the bottom of the wells. In order to avoid the solution to leak, O-seals (Viton) are positioned between the mask and the substrate. After drying at ambient temperature a still loose porous film has formed (b) that is densified by calcination, which leads to better adhesion to the substrate (c).

The tendency of the coatings to form cracks is significantly reduced relative to the direct coating with a sol, since the particle shedding after drying is rather loose and will gain density during the sintering. The magnification from the microscope image shows a homogeneous crack-free film formed by sedimentation, which is independent of the drying process of the suspension (see fig. 3). The high porosity and the large content of macropores formed in these films also guarantee an improved interaction of the atmosphere and its pollutants with the material. Table 2 lists the libraries of the first generation. To guarantee the adhesion of the oxide films on the substrate additional sol of the pure base oxide (except for Sn, and In) was first pipetted into the cavity of synthesis reactor. Here, the content of the base oxide within the sol corresponds to 10% of the oxide quantity of the suspension. This is necessary for metal oxides with a high melting point (e.g. CeO_2 , approx. 2600 °C), since the adhesion on the substrate could not be achieved by sintering alone. Consequently, the libraries with Indium as bulk material were sintered at only 500 °C due to the low melting point of 850 °C. Thus sufficient adhesion was obtained for Indium oxide without adding an adhesive agent. With respect to SnO_2 adding an adhesive agent was advantageous.

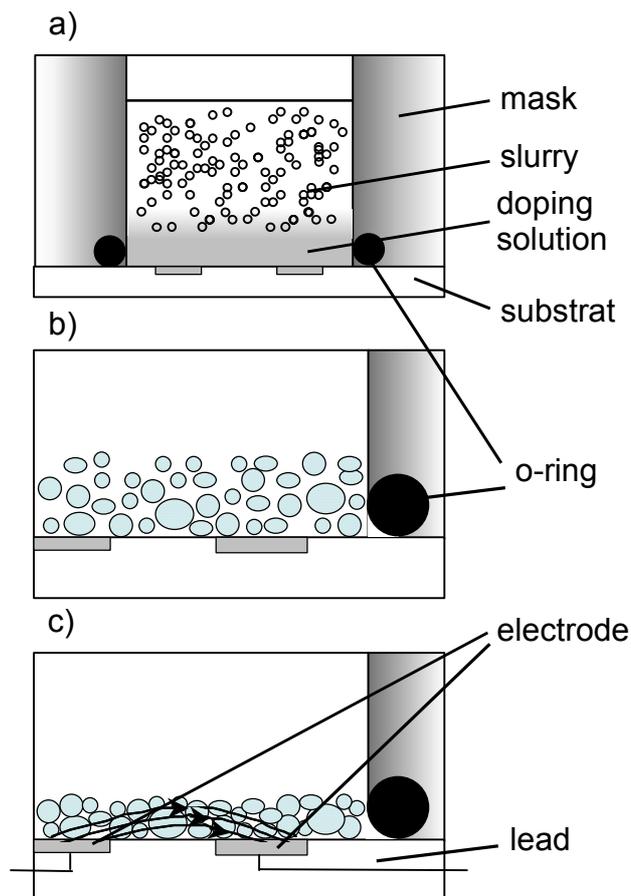


Figure 2. Sequence of the film formation in the synthesis reactor a) after filling in the cavity of the mask, b) after drying c) after calcination.



Figure 3. Light optical microscope image of a WO_3 (left) and ZrO_2 layer (right).

In order to check the IS screening results each sensor was positioned in the respective library three times and the non-doped base material four times. Thus, 21 different materials per material library could be tested. The performance of the IS setup is evaluated by the measurement of a library containing 64 identical films of pure SnO_2 as reference material. All sensors are showing a uniform

response to each test gas. Concerning the gas supply from the central position above the library, the IS response shows a slow decrease from the middle to the outer sensors. To compensate these deviations between different positions on a library, sensors with the same composition are statistically distributed as shown in fig. 4. This layout is used for the synthesis of all libraries.

Table 2. Starting libraries, number of dopants and used primers. The amount of the bulk element in the primer sol corresponds to 10% of the amount in the oxide powder. Libraries are containing bulk- and/or surface dopants.

bulk oxide	libraries	surface-dopants	content [At%]	bulk-dopants	content [At%]	primer
WO ₃	3	40	0.5	20	0.5	10% W-sol
SnO ₂	3	40	0.5	20	0.5	PEG 600
ZrO ₂	1	20	0.5	-	-	10% Zr-sol
TiO ₂	1	20	0.5	-	-	10% Ti-sol
CeO ₂	2	20	0.5	20	0.5	10% Ce-sol
Bi ₂ O ₃	1	20	0.5	-	-	10% Bi-sol
In ₂ O ₃	2	20	0.5	20	0.5	-

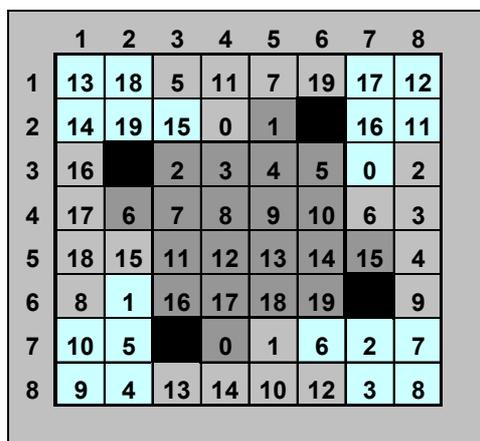


Figure 4. Equal distribution of sensor with 20 different dopants on a library due to the gas flow of the HT-IS setup. Each sensor is deposited three times for reproducing reasons, black fields represent the undoped samples.

It was found that the basic conductivity of sensor libraries with Ce, Bi, Ti, and Zr base oxides was too low due to their high semiconductor band gaps, therefore materials performance could only be carried out via direct current measurements. Introducing bulk dopants did not enhance the basic

conductivity of these materials either. Therefore, these matrix materials could not be used any further. The basic materials W, Sn and In oxide alone showed already sufficient conductivity for IS applications and were consequently selected for further development. The characteristic for evaluation of a suitable sensor material was based on the highest sensitivity for the test gas combined with a cross-sensitivity of less than 10 % to the other gases, which was set with the help of the respective filter options of the data base. In addition, the results were checked for reproducibility by comparing them with the data of the two identical materials on the same substrate. The response of the sensors to the test gases is described by the calculated relative sensitivity [28]. The relative sensitivity is defined as $S = \pm(R_{\max} - R_{\min})/R_{\max}$, with R_{\max} being the maximum and R_{\min} being the minimum resistance of a sensor, measured by HT-IS. The algebraic sign of the sensitivity indicates whether the resistance is enhanced or reduced when supplying a test gas. The results of the HT-IS measurements clearly show that the classical SnO₂-based sensors dispose of very good response properties, but selectivity for a single gas is only found with a few materials for NO₂ relative to NO at low temperatures. Sensors based on indium, and tungsten oxide show with almost all dopants a significant response to the test gas propene. Therefore, the search for a selective sensor that does not show any response or cross-sensitivity for propene was stopped. The sensitivity to the test gases H₂, CO, and NO_x is affected by variation of the temperature as well as variation of the nature of the dopant. The temperature effect is shown in fig. 5 with the response to NO_x on the doped In-oxides. When enhancing the temperature the 0.5 at% surface doped indiumoxide sensor (In_{99,5}Ag_{0,5}O_x) reduces its sensitivity to both NO and NO₂, while the Co-doped material suppresses the sensitivity to H₂ at low temperatures, i.e. at low temperatures the sensor responds selectively to NO_x and at higher temperatures it responds selectively to H₂. The basic conductivity of the base oxide WO₃ is significantly enhanced by using tantalum as bulk dopant. Using yttrium as bulk dopant improves the response properties of WO₃ samples with several surface dopants. The IS measurements of all libraries provided more than 40,000 data records that can be visualized most effectively with the help of the database via hierarchic clustering.

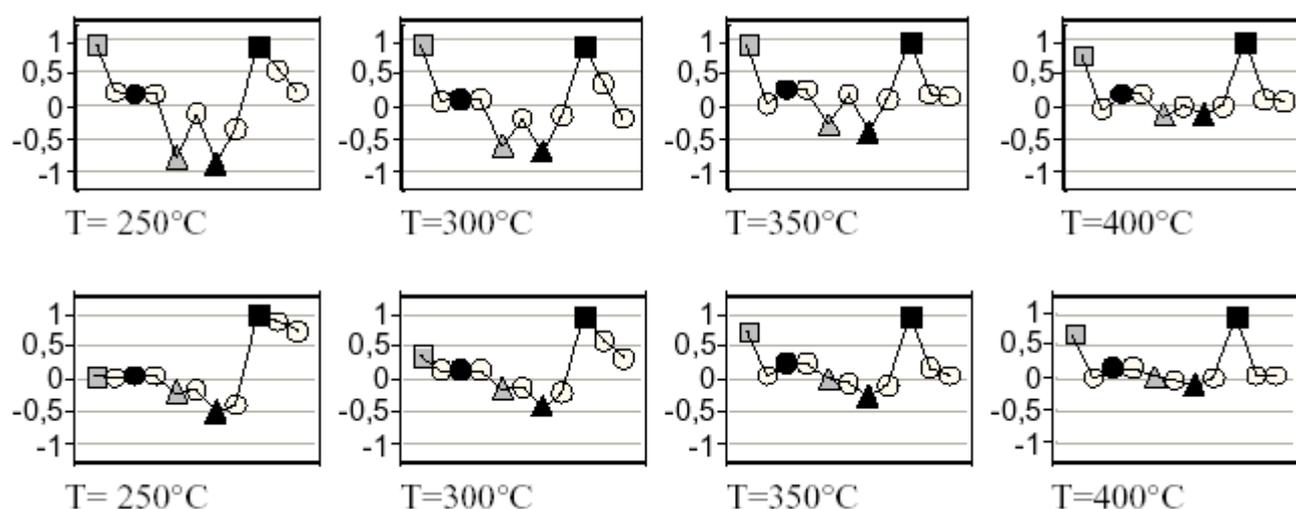


Figure 5. Influence of the temperature to the relative sensitivity S . Sensors: In_{99,5}Ag_{0,5}O_x (above)
 In_{99,5}Co_{0,5}O_x (below): X-Axis: chronology of test gas impact: \square H₂, \bullet CO, \triangle NO, \blacktriangle NO₂,
 \blacksquare propene, \circ synthetic air.

Among the most selective sensor materials found (see table 3) from the IS measurement data with the help of the database, some doped wolfram oxides show a significantly selective response to nitrous dioxide or to propene at a measurement temperature of 300 °C. The sensitivities of these sensors during the sequence of gases in the measurement are represented by the fingerprints shown in fig. 6 or 7 respectively. These fingerprints show the relative responses of the sensor materials to the sequence of test gases. The marked fingerprints belong to materials, which show selective responses.

Table 3. Selection of selective single sensors based on the HT-IS measurements.

bulk doped oxides	test gas	c(gas) [ppm]/ LOD [1/ppm]	selectivity to	temperature [°C]
In _{99,5} Co _{0,5} O _x	NO/NO ₂	5/0.18; 0.26	H ₂ , CO	250
W ₉₉ Co _{0,5} Y _{0,5} O _x ^a	NO ₂	5/0.40	NO, H ₂ , CO	300
W _{98,3} Ta _{0,2} Y ₁ Mg _{0,5} O _x ^b	NO ₂	5/0.17	NO, H ₂ , CO	300
W _{99,5} Ta _{0,5} O _x	Propene	50/2.1·10 ⁻³	all gases	250
W _{99,5} Rh _{0,5} O _x	CO	50/5.2·10 ⁻³	NO, NO ₂	400

^a Co: surface dopant

^b Mg: surface dopant

In addition the variation of the sensors electric resistances has been sequentially measured in the constant current mode using a different high throughput setup [30]. Fig. 8a shows a visualisation of the fingerprints of these measurements of the different sensor materials (9 libraries, with a total of 2112 profiles arranged vertically), whose sensitivities are arranged depending on similarity using hierarchical clustering (vertical axis). The sensitivity profiles are shown in the horizontal axis, where the responses of each material to the previously described sequences of test gases always followed by flushing with synthetic air, is shown at the temperature indicated in the left column. Besides the broad group of materials showing no sensitivities towards all gases, there are areas with response of the sensors to several gases (cross sensitive materials) as well as a few materials, which respond only to one single gas, but do not recover rapidly, as seen in the ongoing response without pollutant (fig. 8a, responses to air). Only sensors showing a selective response toward a single test gas are of interest for a practical application. Cluster areas with high selectivity towards NO or to propene have been extracted from 8a and are shown for clarity in fig. 8b. This map contains only the sensor profiles of fig 8a, showing selective response to one test gas, profiles without selective performance have been filtered by the software. In table 4 further specifications of a selection of sensors belonging to these clusters are given. Particularly yttrium and tantalum doped tungsten oxides with different surface dopants are promising sensor materials for propene, while doped bismuth oxides and undoped tin

oxide seem suitable for the detection of NO. The materials listed in table 3 and 4 are only potential sensor materials (hits). For practical applications, these materials still need to be optimized by known technology until they meet the desired requirements.

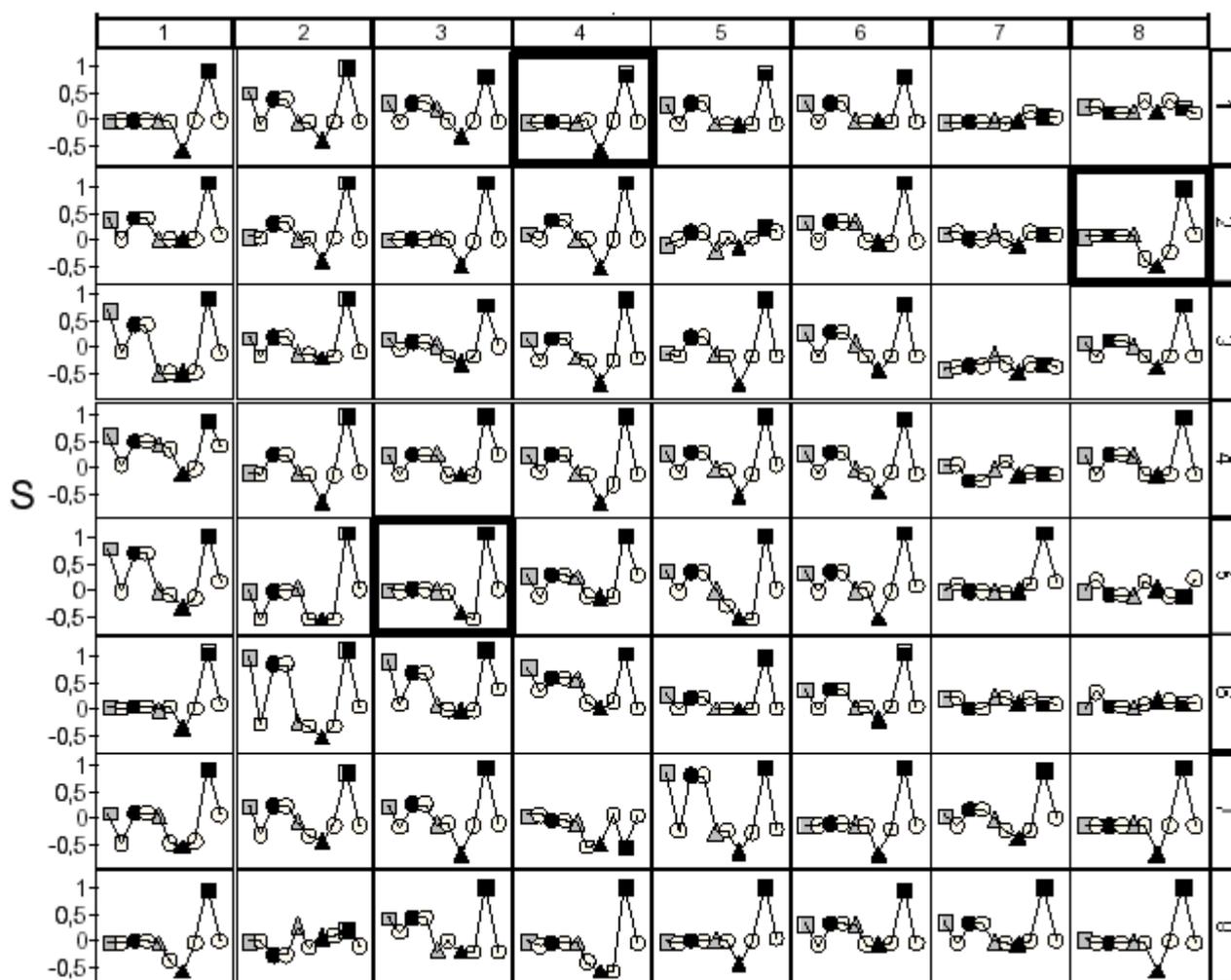


Figure 6. HT-IS screening results of a Ta 0.2 at% and Y 1 at% bulk doped tungsten oxide library at 300°C. Visualisation of the fingerprints using the software Spotfire™.

Y-Axis: sensitivities, X-Axis: chronology of test gas impact: \square H₂, \bullet CO, \triangle NO, \blacktriangle NO₂, \blacksquare propene, \circ synthetic air. Framed sensor material: Mg_{0,5}Ta_{0,2}Y₁W_{98,3}O_x

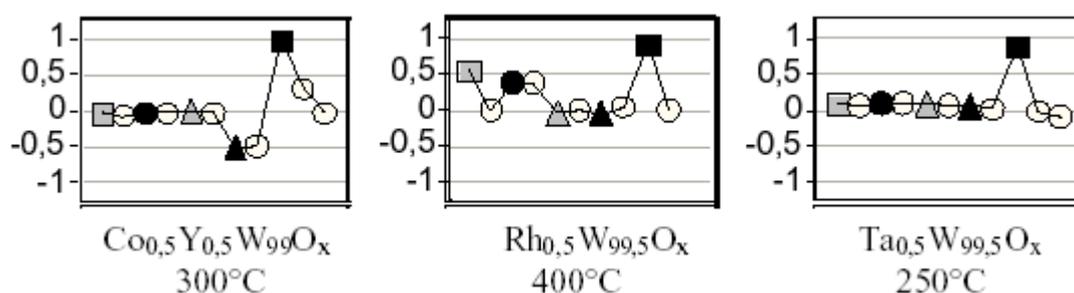


Figure 7. Fingerprints of selected single sensors.

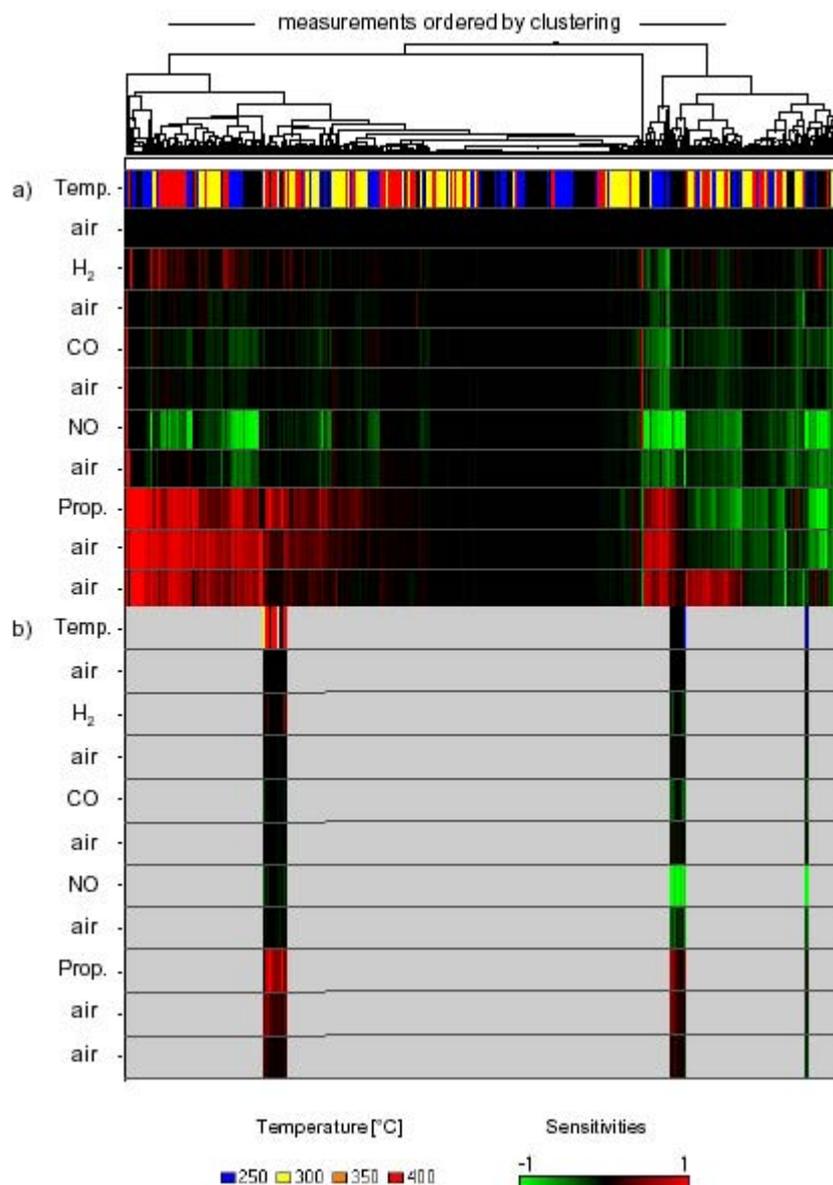


Figure 8. a) Hierarchical clustering map of the sensitivities based on the high-throughput constant current measurements using the data-mining software Spotfire™. Clustering algorithm: 'Complete Linkage' of the Euclidean distances. b) Cluster of high selective sensors towards NO or propene respectively extracted from a).

3.2. Sensormaterials based on mixed oxides

The properties of the sensors was attempted through the formation of mixed oxides, since it is well-known that the formation of new compositions is associated with variation in properties and basic conductivity [13]. An In-W-oxide library with two binary composition spreads with a step-size 10 at% and different bulk dopants was prepared. Such a procedure requires the parallel synthesis of 22 mixed oxides for each system and an optimisation of the adhesion properties and film quality. For the high throughput applications a reduction of each batch was reduced to approx. 60 mg. The automated suspending and stirring was carried out by a pipetting robot in GC vials. For the preparation of the mixed oxide sols stable aqueous In or W stock solutions were prepared, which contained both an organic binding agent and nitric acid. For sol preparation increasing W concentration gradually

improved the gelation process. After sol-preparation and gelation, the materials were dried and calcined in the vials. The resulting mixed oxides were pulverized with a glass rod and used for the preparation of the slurries mentioned above. The adhesion of the films on the support is obtained for single tungsten oxides with and for single indium oxides without a primer (see table 2). Though all slurries of the In-W composition spread were deposited on the library plate without any adhesive agent, only few films showed a tendency to delaminate (see fig. 9). The film quality of the remaining samples is comparable and not dependent on the sensors composition.

Table 4. Examples of high selective materials extracted from the clusters of fig. 8b.

bulk oxide	test gas	temperature [°C]	bulk dopants [0.5 At%]	surface dopants [0.5 At%]
Sn	NO	250-300	-	-
Bi	NO	250-300	-	pure; Er, Sm, Sc, Y
W	propene	350	Y	pure; Au, Co, Cr, Mg, Sc, Eu
	propene	300-400	Ta	pure, Cu
In	propene	350	Ce	-

The potential sensor materials were examined by XRF, which confirmed the expected composition for the Co composition spreads and doped Co-based materials. Minor deviations were found in the samples doped with Th. These are presumably caused by the preparation procedure, since some sols of this composition spread showed a slight clouding during synthesis. Besides the reflexes of the mixed oxide materials the XRD measurements showed signals of the plate material and the platinum electrodes on the plate. The eleven samples of the composition spread indium/tungsten were prepared without doping. An orthorhombic mixed oxide phase $\text{In}_2(\text{WO}_4)_3$ [29] with tungsten contents of 40 through 90 at% and a rhombohedral indium-enriched phase $\text{In}_6\text{WO}_{12}$ [13] with a tungsten content of 20 through 50 at% could be identified as known main phases. Up to a content of approx. 50 at% of W or respectively of In the pure oxides were detectable as additional compounds. Thus, defined indium and tungsten compounds and not just solid solutions in the pure base oxides have been formed. Furthermore, it could be shown that parameters with respect to the technical process such as sintering temperature and time strongly influence the phase characteristics. This is shown when the library is sintered at 700 °C for 7 days since the minor phases disappear and the crystallinity of the materials increases. Therefore, these parameters must be adapted to the operating temperature of the final sensor in order to guarantee a long-term stability. The high throughput synthesis technology of composition spread preparation via application of oxide suspensions is thus a suitable tool for the rapid discovery and development of mixed-oxide materials with new sensor properties for resistive gas sensing applications. Based on the HT-IS measurements, only few compositions qualified for further developments, since the basic conductivity of most materials was too low. Due to this limitation, which is strongly dependent on the mixed oxide composition, the further sensor optimisation is restricted to materials containing only one single oxide.

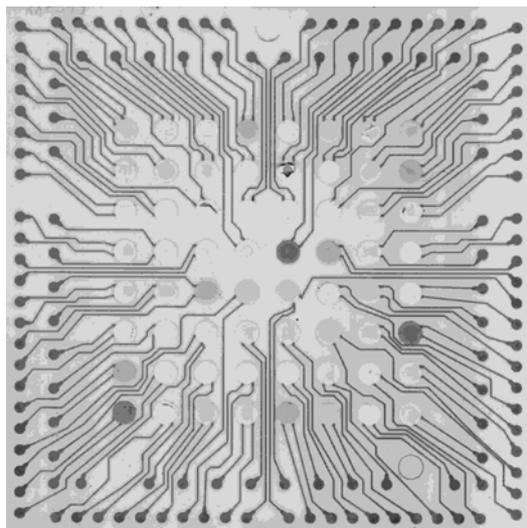


Figure 9. Image of the In/W mixed oxide library.

4. Summary and Conclusion

Based on combinatorial procedures a simple synthesis method for creating thick porous metal oxide films within the range of approx. 10-20 μm has been developed. Seven different base oxides were selected, which were used to generate homogeneous films by implementing respectively bulk and/or surface dopants as well as adhesive agents. Advantage of this synthesis strategy is the easy application to other metal oxide by proper selection of the adhesive agent. The resulting films were optimised with respect to their characteristics as resistive gas sensors. The materials were ranked according to performance under identical sensing conditions. By variation of the doping elements both the base conductivity of the materials and the cross-sensitivities to other gases under HT-conditions could be improved. It has been shown, that with miniaturizing and parallelizing procedures it is possible to generate mixed-oxide sensor libraries, which can be screened rapidly for gas sensing properties. The method presented allows to rapidly screen large parameter spaces of composition and preparation processes for potential new resistive gas sensor materials. The materials discovered still have to be optimized, characterized and adapted for practical applications and commercialization. Here optimisation means optimizing the materials preparation for improved performance, reproducibility and stability under realistic sensing conditions. Characterization should target to understand the effect of the dopants and microstructure on the sensing properties. It should also clarify the phase composition, the homogeneity of the chemical composition and the chemical neighbourhood and oxidation states of the active elements.

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